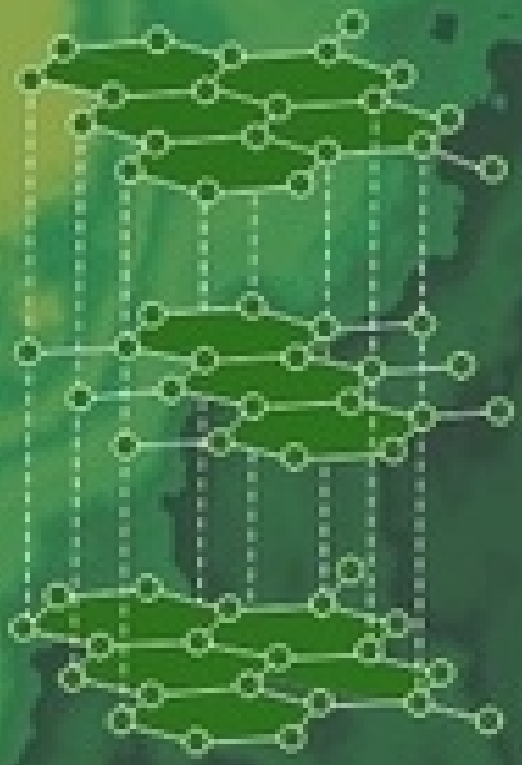
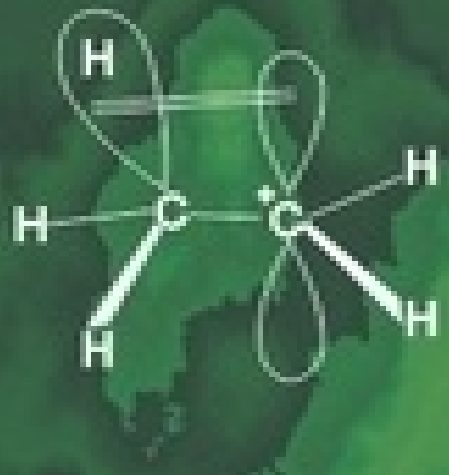
Textbook for Class XI



Chemistry

Part I

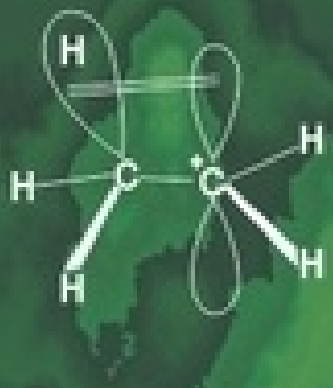


Textbook for Class XI

Unit 1
Some Basic Concepts of Chemistry

Chemistry

Part I



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Unit 1

Some Basic Concepts of Chemistry

Objectives

After studying this unit, you will be able to

- appreciate the contribution of India in the development of chemistry understand the role of chemistry in different spheres of life;
- explain the characteristics of three states of matter;
- classify different substances into elements, compounds and mixtures;
- use scientific notations and determine significant figures;
- differentiate between precision and accuracy;
- define SI base units and convert physical quantities from one system of units to another;
- explain various laws of chemical combination;
- appreciate significance of atomic mass, average atomic mass, molecular mass and formula mass;
- describe the terms – mole and molar mass;
- calculate the mass per cent of component elements constituting a compound;
- determine empirical formula and molecular formula for a compound from the given experimental data; and

- perform the stoichiometric calculations.

"Chemistry is the science of molecules and their transformations. It is the science not so much of the one hundred elements but of the infinite variety of molecules that may be built from them."

Roald Hoffmann

Science can be viewed as a continuing human effort to systematise knowledge for describing and understanding nature. You have learnt in your previous classes that we come across diverse substances present in nature and changes in them in daily life. Curd formation from milk, formation of vinegar from sugarcane juice on keeping for prolonged time and rusting of iron are some of the examples of changes which we come across many times. For the sake of convenience, science is sub-divided into various disciplines: chemistry, physics, biology, geology, etc. The branch of science that studies the preparation, properties, structure and reactions of material substances is called chemistry.

Development of chemistry

Chemistry, as we understand it today, is not a very old discipline. Chemistry was not studied for its own sake, rather it came up as a result of search for two interesting things:

i. Philosopher's stone (Paras) which would convert all baser metals e.g., iron and copper into gold.

ii. 'Elexir of life' which would grant immortality.

People in ancient India, already had the knowledge of many scientific phenomenon much before the advent of modern science. They applied that knowledge in various walks of life. Chemistry developed mainly in the form of Alchemy and Iatrochemistry during 1300-1600 CE. Modern

chemistry took shape in the 18th century Europe, after a few centuries of alchemical traditions which were introduced in Europe by the Arabs.

Other cultures – especially the Chinese and the Indian – had their own alchemical traditions. These included much knowledge of chemical processes and techniques. In ancient India, chemistry was called Rasayan Shastra, Rastantra, Ras Kriya or Rasvidya. It included metallurgy, medicine, manufacture of cosmetics, glass, dyes, etc. Systematic excavations at Mohenjodaro in Sindh and Harappa in Punjab prove that the story of development of chemistry in India is very old. Archaeological findings show that baked bricks were used in construction work. It shows the mass production of pottery, which can be regarded as the earliest chemical process, in which materials were mixed, moulded and subjected to heat by using fire to achieve desirable qualities. Remains of glazed pottery have been found in Mohenjodaro. Gypsum cement has been used in the construction work. It contains lime, sand and traces of $CaCO_3$. Harappans made faience, a sort of glass which was used in ornaments. They melted and forged a variety of objects from metals, such as lead, silver, gold and copper. They improved the hardness of copper for making artefacts by using tin and arsenic. A number of glass objects were found in Maski in South India (1000–900 BCE), and Hastinapur and Taxila in North India (1000–200 BCE). Glass and glazes were coloured by addition of colouring agents like metal oxides.

Copper metallurgy in India dates back to the beginning of chalcolithic cultures in the

subcontinent. There are much archeological evidences to support the view that technologies for extraction of copper and iron were developed indigenously.

According to Rigveda, tanning of leather and dying of cotton were

practised during 1000–400 BCE. The golden gloss of the black polished ware of northen India could not be replicated and is still a chemical mystery. These wares indicate the mastery with which kiln temperatures could be controlled. Kautilya's Arthashastra describes the production of salt from sea.

A vast number of statements and material described in the ancient Vedic literature can be shown to agree with modern scientific findings. Copper utensils, iron, gold, silver ornaments and terracotta discs and painted grey pottery have been found in many archaeological sites in north India. Sushruta Samhita explains the importance of Alkalies. The Charaka Samhita mentions ancient indians who knew how to prepare sulphuric acid, nitric acid and oxides of copper, tin and zinc; the sulphates of copper, zinc and iron and the carbonates of lead and iron.

Rasopanishada describes the preparation of gunpowder mixture. Tamil texts also describe the preparation of fireworks using sulphur, charcoal, saltpetre (i.e., potassium nitrate), mercury, camphor, etc.

Nagarjuna was a great Indian scientist. He was a reputed chemist, an alchemist and a metallurgist. His work Rasratnakar deals with the formulation of mercury compounds. He has also discussed methods for the extraction of metals, like gold, silver, tin and copper. A book, Rsarnavam, appeared around 800 CE. It discusses the uses of various furnaces, ovens and crucibles for different purposes. It describes methods by which metals could be identified by flame colour.

Chakrapani discovered mercury sulphide. The credit for inventing soap also goes to him. He used mustard oil and some alkalies as ingredients for making soap. Indians began making soaps in the 18^{th} century CE. Oil of Eranda and seeds of Mahua plant and calcium carbonate were used for making soap.

The paintings found on the walls of Ajanta and Ellora, which look fresh

even after ages, testify to a high level of science achieved in ancient India. Varähmihir's Brihat Samhita is a sort of encyclopaedia, which was composed in the sixth century CE. It informs about the preparation of glutinous material to be applied on walls and roofs of houses and temples. It was prepared entirely from extracts of various plants, fruits, seeds and barks, which were concentrated by boiling, and then, treated with various resins. It will be interesting to test such materials scientifically and assess them for use.

A number of classical texts, like Atharvaveda (1000 BCE) mention some dye stuff, the material used were turmeric, madder, sunflower, orpiment, cochineal and lac. Some other substances having tinting property were kamplcica, pattanga and jatuka.

Varähmihir's Brihat Samhita gives references to perfumes and cosmetics. Recipes for hair dying were made from plants, like indigo and minerals like iron power, black iron or steel and acidic extracts of sour rice gruel. Gandhayukli describes recipes for making scents, mouth perfumes, bath powders, incense and talcum power.

Paper was known to India in the17th century as account of Chinese traveller

I-tsing describes. Excavations at Taxila indicate that ink was used in India from the fourth century. Colours of ink were made from chalk, red lead and minimum.

It seems that the process of fermentation was well-known to Indians. Vedas and Kautilya's Arthashastra mention about many types of liquors. Charaka Samhita also mentions ingredients, such as barks of plants, stem, flowers, leaves, woods, cereals, fruits and sugarcane for making Asavas.

The concept that matter is ultimately made of indivisible building blocks, appeared in India a few centuries BCE as a part of philosophical

speculations. Acharya Kanda, born in 600 BCE, originally known by the name Kashyap, was the first proponent of the ‘atomic theory’. He formulated the theory of very small indivisible particles, which he named ‘Paramãnu’ (comparable to atoms). He authored the text Vaiseshika Sutras. According to him, all substances are aggregated form of smaller units called atoms (Paramãnu), which are eternal, indestructible, spherical, suprasensible and in motion in the original state. He explained that this individual entity cannot be sensed through any human organ. Kanda added that there are varieties of atoms that are as different as the different classes of substances. He said these (Paramãnu) could form pairs or triplets, among other combinations and unseen forces cause interaction between them. He conceptualised this theory around 2500 years before John Dalton (1766-1844).

Charaka Samhita is the oldest Ayurvedic epic of India. It describes the treatment of diseases. The concept of reduction of particle size of metals is clearly discussed in Charaka Samhita. Extreme reduction of particle size is termed as nanotechnology. Charaka Samhita describes the use of bhasma of metals in the treatment of ailments. Now-a-days, it has been proved that bhasmas have nanoparticles of metals.

After the decline of alchemy, Iatrochemistry reached a steady state, but it too declined due to the introduction and practise of western medicinal system in the 20^{th} century. During this period of stagnation, pharmaceutical industry based on Ayurveda continued to exist, but it too declined gradually. It took about 100-150 years for Indians to learn and adopt new techniques. During this time, foreign products poured in. As a result, indigenous traditional techniques gradually declined. Modern science appeared in Indian scene in the later part of the nineteenth century. By the mid-nineteenth century, European scientists started coming to India and modern chemistry started growing.

From the above discussion, you have learnt that chemistry deals with the composition, structure, properties and interection of matter and is of much use to human beings in daily life. These aspects can be best described and understood in terms of basic constituents of matter that are **atoms** and **molecules**. That is why, chemistry is also called the science of atoms and molecules. Can we see, weigh and perceive these entities (atoms and molecules)? Is it possible to count the number of atoms and molecules in a given mass of matter and have a quantitative relationship between the mass and the number of these particles? We will get the answer of some of these questions in this Unit. We will further describe how physical properties of matter can be quantitatively described using numerical values with suitable units.

1.1 IMPORTANCE OF CHEMISTRY

Chemistry plays a central role in science and is often intertwined with other branches of science.

Principles of chemistry are applicable in diverse areas, such as weather patterns, functioning of brain and operation of a computer, production in chemical industries, manufacturing fertilisers, alkalis, acids, salts, dyes, polymers, drugs, soaps, detergents, metals, alloys, etc., including new material.

Chemistry contributes in a big way to the national economy. It also plays an important role in meeting human needs for food, healthcare products and other material aimed at improving the quality of life. This is exemplified by the large-scale production of a variety of fertilisers, improved variety of pesticides and insecticides. Chemistry provides methods for the isolation of life-saving drugs from natural sources and makes possible synthesis of such drugs. Some of these drugs are **cisplatin** and **taxol**, which are effective in cancer therapy. The drug AZT (Azidothymidine) is used for helping AIDS patients.

Chemistry contributes to a large extent in the development and growth of a nation. With a better understanding of chemical principles it has now become possible to design and synthesise new material having specific magnetic, electric and optical properties. This has lead to the production of superconducting ceramics, conducting polymers, optical fibres, etc. Chemistry has helped in establishing industries which manufacture utility goods, like acids, alkalies, dyes, polymesr metals, etc. These industries contribute in a big way to the economy of a nation and generate employment.

In recent years, chemistry has helpedin dealing with some of the pressing aspectsof environmental degradation with a fair degree of success. Safer alternatives to environmentally hazardous refrigerants, like CFCs (chlorofluorocarbons), responsible for ozone depletion in the stratosphere, have been successfully synthesised. However, many big environmental problems continue to be matters of grave concern to the chemists. One such problem is the management of the Green House gases, like methane, carbon dioxide, etc. Understanding of biochemical processes, use of enzymes for large-scale production of chemicals and synthesis of new exotic material are some of the intellectual challenges for the future generation of chemists. A developing country, like India, needs talented and creative chemists for accepting such challenges. To be a good chemist and to accept such challanges, one needs to understand the basic concepts of chemistry, which begin with the concept of matter. Let us start with the nature of matter.

1.2 Nature of Matter

You are already familiar with the term **matter** from your earlier classes. Anything which has mass and occupies space is called **matter**. Everything around us, for example, book, pen, pencil, water, air, all living beings, etc., are composed of matter. You know that they have mass and

they occupy space. Let us recall the characteristics of the states of matter, which you learnt in your previous classes.

1.2.1 States of Matter

You are aware that matter can exist in three physical states viz. **solid**, **liquid** and **gas**. The constituent particles of matter in these three states can be represented as shown in Fig. 1.1.

Particles are held very close to each other in **solids** in an orderly fashion and there is not much freedom of movement. In **liquids**, the particles are close to each other but they can move around. However, in **gases**, the particles are far apart as compared to those present in solid or liquid states and their movement is easy and fast. Because of such arrangement of particles, different states of matter exhibit the following characteristics:

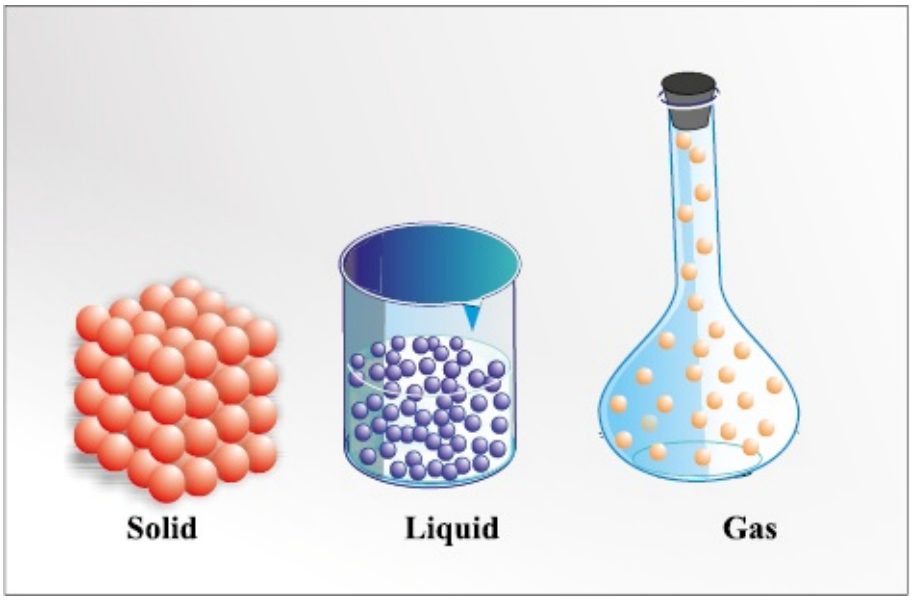


Fig. 1.1 Arrangement of particles in solid, liquid and gaseous state

(i) Solids have definite volume and definite shape.

(ii) Liquids have definite volume but do not have definite shape. They take the shape of the container in which they are placed.

(iii) Gases have neither definite volume nor definite shape. They

completely occupy the space in the container in which they are placed. These three states of matter are interconvertible by changing the conditions of temperature and pressure.

Solid $\underset{\text{cool}}{\overset{\text{heat}}{\rightleftharpoons}}$ liquid $\underset{\text{cool}}{\overset{\text{heat}}{\rightleftharpoons}}$ Gas

On heating, a solid usually changes to a liquid, and the liquid on further heating changes to gas (or vapour). In the reverse process, a gas on cooling liquifies to the liquid and the liquid on further cooling freezes to the solid.

1.2.2. Classification of Matter

In class IX (Chapter 2), you have learnt that at the macroscopic or bulk level, matter can be classified as **mixture** or **pure substance**. These can be further sub-divided as shown in Fig. 1.2.

When all constituent particles of a substance are same in chemical nature, it is said to be a pure substance. A mixture contains many types of particles.

A mixture contains particles of two or more pure substances which may be present in it in any ratio. Hence, their composition is variable. Pure sustances forming mixture are called its components. Many of the substances present around you are **mixtures**. For example, sugar solution in water, air, tea, etc., are all mixtures. A mixture may be **homogeneous** or **heterogeneous**. In a **homogeneous mixture**, the components completely mix with each other. This means particles of components of the mixture are uniformly distributed throughout the bulk of the mixture and its composition is uniform throughout. Sugar solution and air are the examples of homogeneous mixtures. In contrast to this, in a **heterogeneous mixture**, the composition is not uniform throughout and sometimes different components are visible. For example, mixtures of salt and sugar, grains and pulses along with some dirt (often stone pieces), are heterogeneous mixtures. You can think of many more

examples of mixtures which you come across in the daily life. It is worthwhile to mention here that the components of a mixture can be separated by using physical methods, such as simplehand-picking, filtration, crystallisation, distillation, etc.

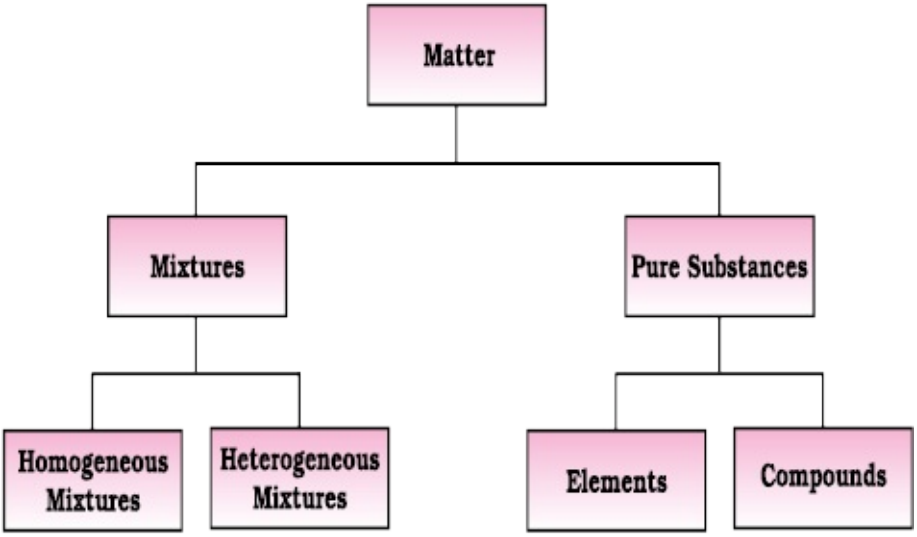


Fig. 1.2 Classification of matter

Pure substances have characteristics different from mixtures. Constituent particles of pure substances have fixed composition. Copper, silver, gold, water and glucose are some examples of pure substances. Glucose contains carbon, hydrogen and oxygen in a fixed ratio and its particles are of same composition. Hence, like all other pure substances, glucose has a fixed composition. Also, its constituents—carbon, hydrogen and oxygen—cannot be separated by simple physical methods. Pure substances can further be classified into **elements** and **compounds**. Particles of an **element** consist of only one type of atoms. These particles may exist as **atoms** or **molecules**. You may be familiar with atoms and molecules from the previous classes; however, you will be studying about them in detail in Unit 2. Sodium, copper, silver, hydrogen, oxygen, etc., are some examples of elements. Their all atoms are of one type. However, the atoms of different elements are different in

nature. Some elements, such as sodium or copper, contain atoms as their constituent particles, whereas, in some others, the constituent particles are molecules which are formed by two or more atoms. For example, hydrogen, nitrogen and oxygen gases consist of molecules, in which two atoms combine to give their respective molecules. This is illustrated in Fig. 1.3.

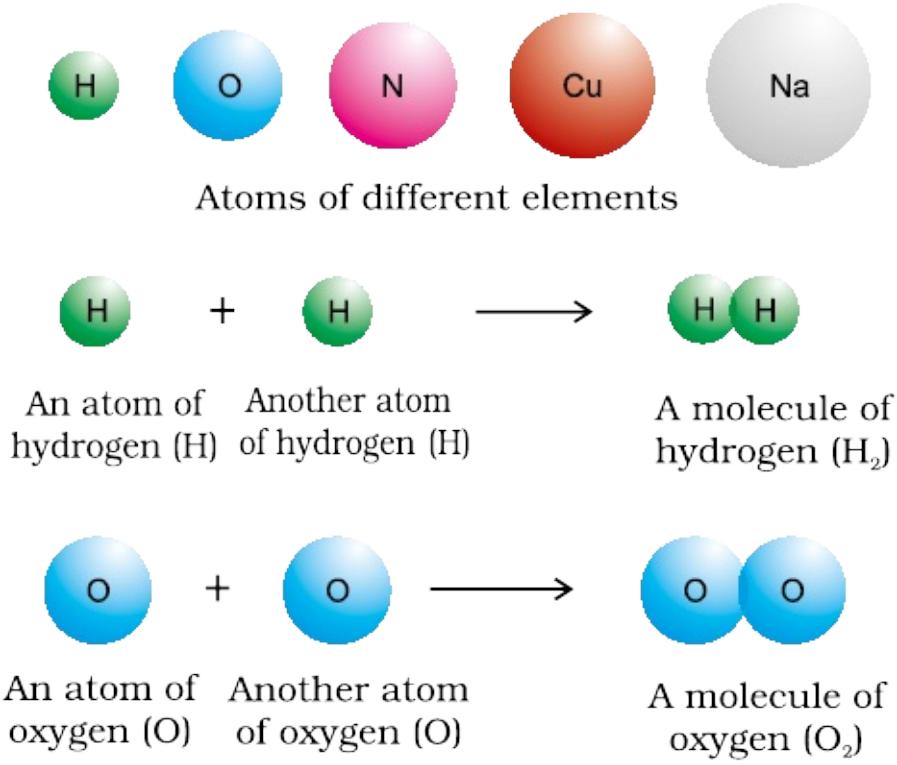


Fig. 1.3 A representation of atoms and molecules

When two or more atoms of different elements combine together in a definite ratio, the molecule of a **compound** is obtained. Moreover, the constituents of a compound cannot be separated into simpler substances by physical methods. They can be separated by chemical methods. Examples of some compounds are water, ammonia, carbon dioxide, sugar, etc. The molecules of water and carbon dioxide are represented in Fig. 1.4.

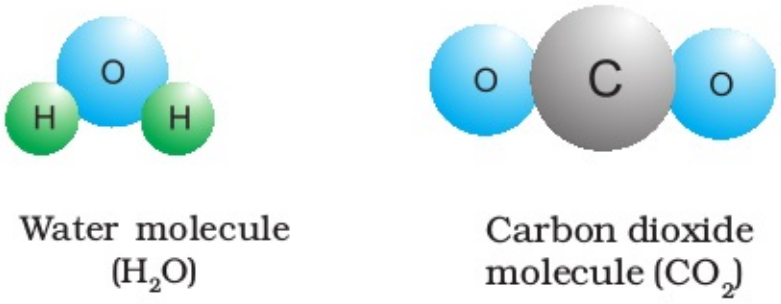


Fig. 1.4 A depiction of molecules of water and carbon dioxide

Note that a water molecule comprises two hydrogen atoms and one oxygen atom. Similarly, a molecule of carbon dioxide contains two oxygen atoms combined with one carbon atom. Thus, the atoms of different elements are present in a compound in a fixed and definite ratio and this ratio is characteristic of a particular compound. Also, the properties of a compound are different from those of its constituent elements. For example, hydrogen and oxygen are gases, whereas, the compound formed by their combination i.e., water is a liquid. It is interesting to note that hydrogen burns with a pop sound and oxygen is a supporter of combustion, but water is used as a fire extinguisher.

1.3 Properties of Matter and their Measurement

1.3.1 Physical and chemical properties

Every substance has unique or characteristic properties. These properties can be classified into two categories — **physical properties,** such as colour, odour, melting point, boiling point, density, etc., and **chemical properties,** like composition, combustibility, ractivity with acids and bases, etc.

Physical properties can be measured or observed without changing the identity or the composition of the substance. The measurement or observation of **chemical properties** requires a chemical change to occur. Measurement of physical properties does not require occurance of a chemical change. The examples of chemical properties are

characteristic reactions of different substances; these include acidity or basicity, combustibility, etc. Chemists describe, interpret and predict the behaviour of substances on the basis of knowledge of their physical and chemical properties, which are determined by careful measurement and experimentation. In the following section, we will learn about the measurement of physical properties.

1.3.2 Measurement of physical properties

Quantitative measurement of properties is reaquired for scientific investigation. Many properties of matter, such as length, area, volume, etc., are quantitative in nature. Any quantitative observation or measurement is represented by a number followed by units in which it is measured. For example, length of a room can be represented as 6 m; here, 6 is the number and m denotes metre, the unit in which the length is measured.

Earlier, two different systems of measurement, i.e., the **English System** and the **Metric System** were being used in different parts of the world. The metric system, which originated in France in late eighteenth century, was more convenient as it was based on the decimal system. Late, need of a common standard system was felt by the scientific community. Such a system was established in 1960 and is discussed in detail below.

Maintaining the National

Standards of Measurement

The system of units, including unit definitions, keeps on changing with time. Whenever the accuracy of measurement of a particular unit was enhanced substantially by adopting new principles, member nations of metre treaty (signed in 1875), agreed to change the formal definition of that unit. Each modern industrialised country, including India, has a National Metrology Institute (NMI), which maintains standards of measurements. This responsibility has been given to the National Physical Laboratory (NPL),

New Delhi. This laboratory establishes experiments to realise the base units and derived units of measurement and maintains National Standards of Measurement. These standards are periodically inter-compared with standards maintained at other National Metrology Institutes in the world, as well as those, established at the International Bureau of Standards in Paris.

1.3.3 The International System of Units (SI)

The International System of Units (in French Le Systeme International d'Unités — abbreviated as SI) was established by the11th General Conference on Weights and Measures (CGPM from ConferenceGenerale des Poids et Measures). The CGPM is an inter-governmental treaty organisation created by a diplomatic treaty known as Metre Convention, which was signed in Paris in 1875.

Table 1.1 Base Physical Quantities and their Units

Base Physical Quantity	Symbol for Quantity	Name of SI Unit	Symbol for SI Unit
Length	l	metre	m
Mass	m	kilogram	kg
Time	t	second	s
Electric current	I	ampere	A
Thermodynamic temperature	T	kelvin	K
Amount of substance	n	mole	mol
Luminous intensity	I_v	candela	cd

The SI system has seven base units and they are listed in Table 1.1. These units pertain to the seven fundamental scientific quantities. The other physical quantities, such as speed, volume, density, etc., can be derived from these quantities.

The definitions of the SI base units are given in Table 1.2.

Let us now quickly go through some of the quantities which you will be often using in this book.

Table 1.2 Definitions of SI Base Units

Unit of length	**metre**	The *metre* is the length of the path travelled by light in vacuum during a time interval of 1/299 792 458 of a second.
Unit of mass	**kilogram**	The *kilogram* is the unit of mass; it is equal to the mass of the international prototype of the kilogram.
Unit of time	**second**	The *second* is the duration of 9 192 631 770 periods of the radiation corresponding to the transition between the two hyperfine levels of the ground state of the caesium-133 atom.
Unit of electric current	**ampere**	The *ampere* is that constant current, which if maintained in two straight parallel conductors of infinite length of negligible circular cross-section and placed 1 metre apart in vacuum, would produce between these conductors a force equal to 2×10^{-7} newton per metre of length.
Unit of thermodynamic temperature	**kelvin**	The *kelvin*, unit of thermodynamic temperature, is the fraction 1/273.16 of the thermodynamic temperature of the triple* point of water.
Unit of amount of substance	**mole**	1. The *mole* is the amount of substance of a system, which contains as many elementary entities as there are atoms in 0.012 kilogram of carbon-12; its symbol is 'mol'. 2. When the mole is used, the elementary entities must be specified and these may be atoms, molecules, ions, electrons, other particles, or specified groups of such particles.
Unit of luminous intensity	**candela**	The *candela* is the luminous intensity, in a given direction, of a source that emits monochromatic radiation of frequency 540×10^{12} hertz and that has a radiant intensity in that direction of 1/683 watt per steradian.

**Triple point of water is 0.01 °C or 279.16K (32.01 ° F)*

Table 1.3 Prefixes used in the SI System

Multiple	Prefix	Symbol
10^{-24}	yocto	y
10^{-21}	zepto	z
10^{-18}	atto	a
10^{-15}	femto	f
10^{-12}	pico	p
10^{-9}	nano	n
10^{-6}	micro	μ
10^{-3}	milli	m
10^{-2}	centi	c
10^{-1}	deci	d
10	deca	da
10^{2}	hecto	h
10^{3}	kilo	k
10^{6}	mega	M
10^{9}	giga	G
10^{12}	tera	T
10^{15}	peta	P
10^{18}	exa	E
10^{21}	zeta	Z
10^{24}	yotta	Y

The SI system allows the use of prefixes to indicate the multiples or submultiples of a unit. These prefixes are listed in Table 1.3.

1.3.4 Mass and Weight

Mass of a substance is the amount of matter present in it, while **weight** is the force exerted by gravity on an object. The mass of a substance is constant, whereas, its weight may vary from one place to another due to change in gravity. You should be careful in using these terms.

The mass of a substance can be determined accurately in the laboratory by using an analytical balance (Fig. 1.5).

The SI unit of mass as given in Table 1.1 is kilogram. However, its

fraction named as gram (1 kg = 1000 g), is used in laboratories due to the smaller amounts of chemicals used in chemical reactions.

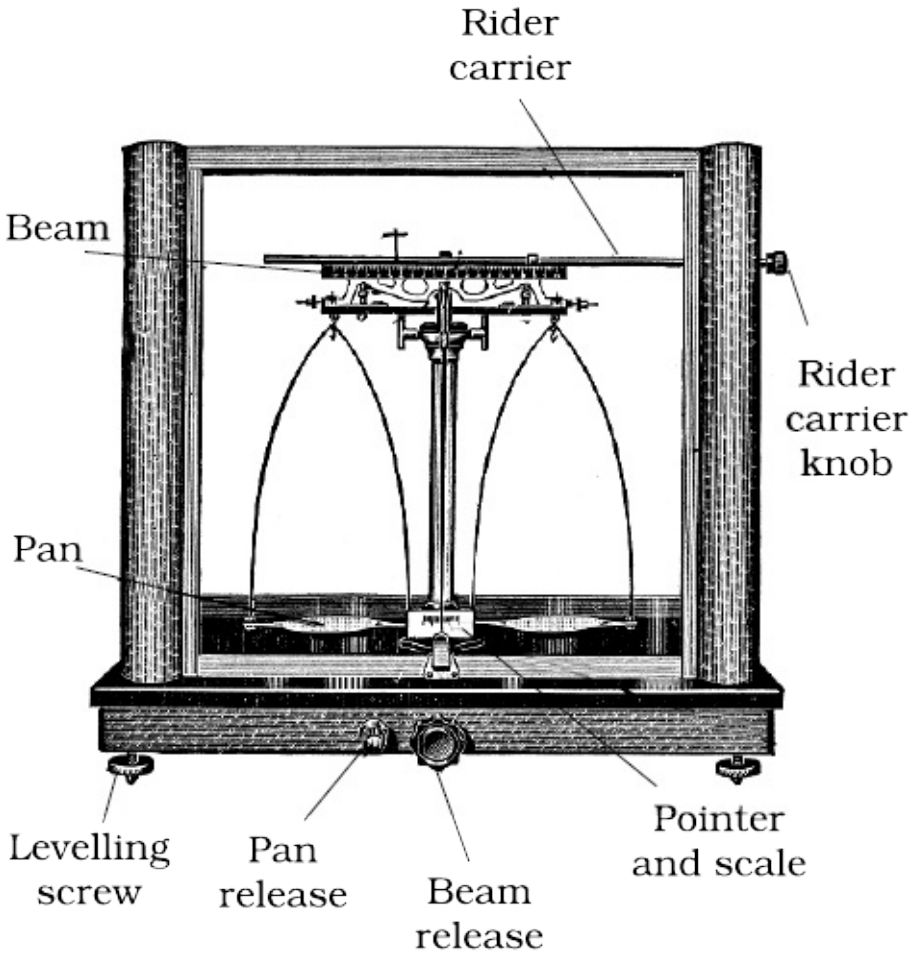


Fig. 1.5 Analytical balance

1.3.5 Volume

Volume is the amont of space occupied by a substance. It has the units of (length)^3. So in SI system, volume has units of m^3. But again, in chemistry laboratories, smaller volumes are used. Hence, volume is often denoted in cm^3 or dm^3 units.

Fig. 1.6 helps to visualise these relations.

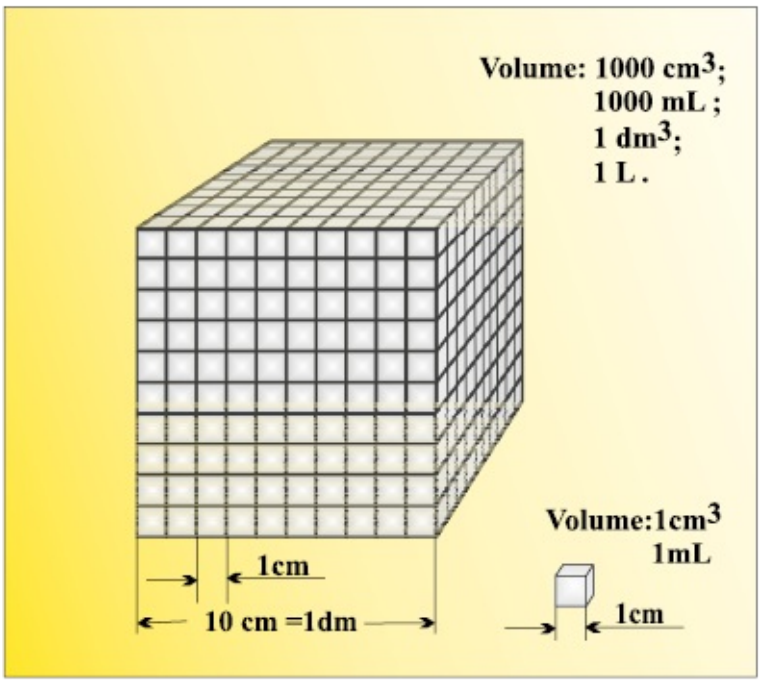


Fig. 1.6 Different units used to express volume

A common unit, litre (L) which is not an SI unit, is used for measurement of volume of liquids.

1 L = 1000 mL , 1000 cm^3 = 1 dm^3

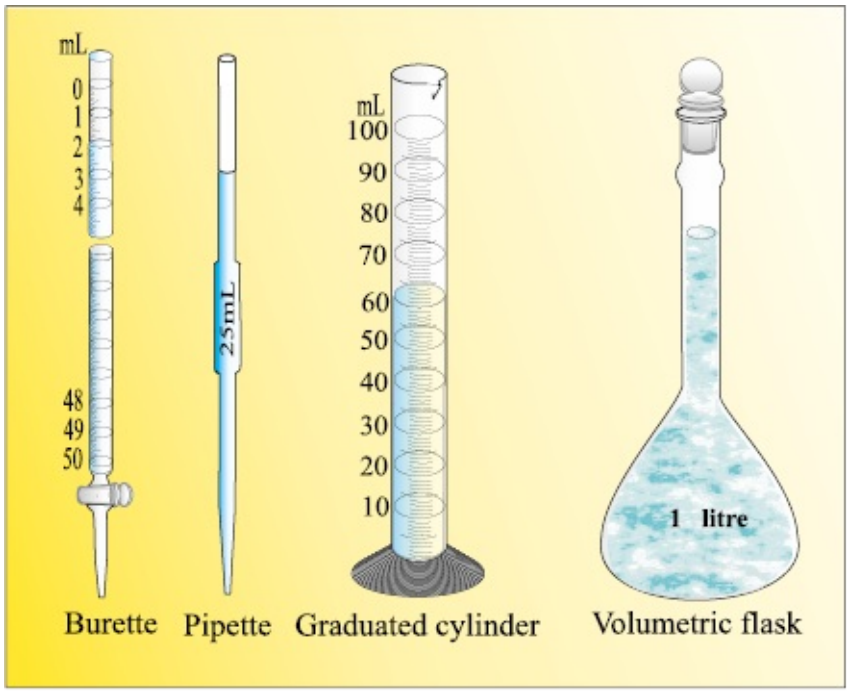


Fig. 1.7 Some volume measuring devices

In the laboratory, the volume of liquids or solutions can be measured by graduated cylinder, burette, pipette, etc. A volumetric flask is used to prepare a known volume of a solution. These measuring devices are shown in Fig. 1.7.

1.3.6 Density

The two properties — mass and volume discussed above are related as follows:

$$\text{Density} = \frac{\text{Mass}}{\text{Volume}}$$

Density of a substance is its amount of mass per unit volume. So, SI units of density can be obtained as follows:

$$\text{SI unit of density} = \frac{\text{SI unit of mass}}{\text{SI unit of volume}}$$

$$= \frac{\text{kg}}{\text{m}^3} \text{ or kg m}^{-3}$$

This unit is quite large and a chemist often expresses density in g cm^{-3}, where mass is expressed in gram and volume is expressed in cm^3. Density of a substance tells us about how closely its particles are packed. If density is more, it means particles are more closely packed.

1.3.7 Temperature

There are three common scales to measure temperature — °C (degree celsius), °F (degree fahrenheit) and K (kelvin). Here, K is the SI unit. The thermometers based on these scales are shown in Fig. 1.8. Generally, the thermometer with celsius scale are calibrated from 0° to 100°, where these two temperatures are the freezing point and the boiling point of water, respectively. The fahrenheit scale is represented between 32° to 212°.

The temperatures on two scales are related to each other by the following relationship:

$$°F = \frac{9}{5}(°C) + 32$$

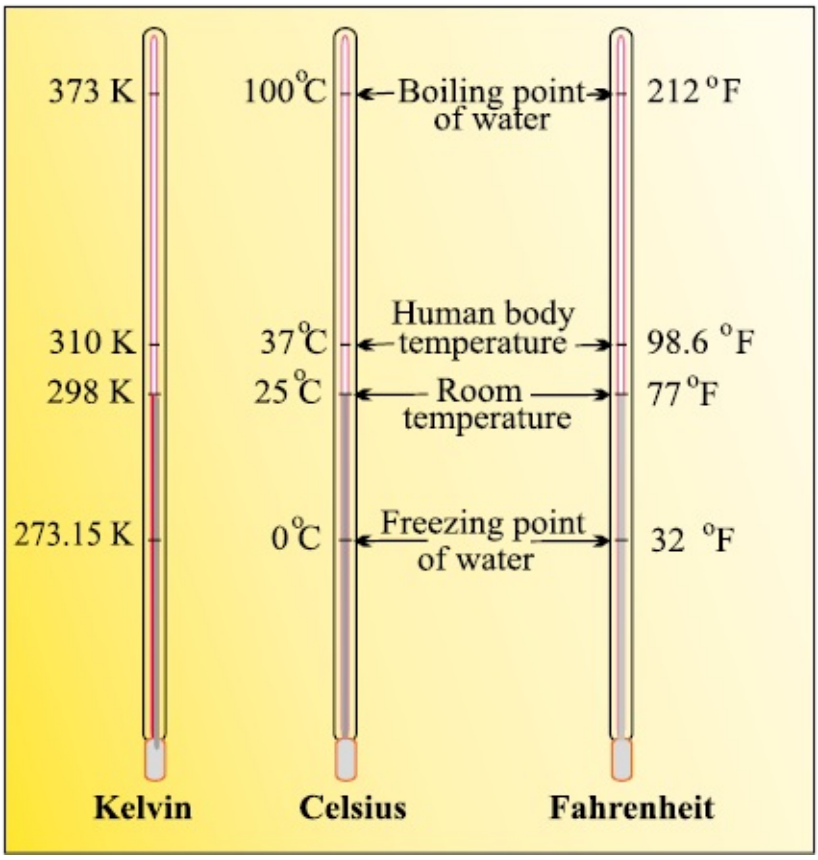


Fig. 1.8 Thermometers using different temperature scales

The kelvin scale is related to celsius scale as follows:

K = °C + 273.15

It is interesting to note that temperature below 0 °C (i.e., negative values) are possible in Celsius scale but in Kelvin scale, negative temperature is not possible.

Reference Standard

After defining a unit of measurement such as the kilogram or the metre, scientists agreed on reference standards that make it possible to calibrate all measuring devices. For getting reliable measurements, all devices such as metre sticks and analytical balances have been calibrated by their manufacturers to give correct readings. However, each of these devices is

standardised or calibrated against some reference. The mass standard is the kilogram since 1889. It has been defined as the mass of platinum-iridium (Pt-Ir) cylinder that is stored in an airtight jar at International Bureau of Weights and Measures in Sevres, France. Pt-Ir was chosen for this standard because it is highly resistant to chemical attack and its mass will not change for an extremely long time.

Scientists are in search of a new standard for mass. This is being attempted through accurate determination of Avogadro constant. Work on this new standard focuses on ways to measure accurately the number of atoms in a well-defined mass of sample. One such method, which uses X-rays to determine the atomic density of a crystal of ultrapure silicon, has an accuracy of about 1 part in 10^6 but has not yet been adopted to serve as a standard. There are other methods but none of them are presently adequate to replace the Pt-Ir cylinder. No doubt, changes are expected within this decade.

The metre was originally defined as the length between two marks on a Pt-Ir bar kept at a temperature of 0°C (273.15 K). In 1960 the length of the metre was defined as 1.65076373×10^6 times the wavelength of light emitted by a krypton laser. Although this was a cumbersome number, it preserved the length of the metre at its agreed value. The metre was redefined in 1983 by CGPM as the length of path travelled by light in vacuum during a time interval of 1/299 792 458 of a second. Similar to the length and the mass, there are reference standards for other physical quantities.

1.4 Uncertainty in Measurement

Many a time in the study of chemistry, one has to deal with experimental data as well as theoretical calculations. There are meaningful ways to handle the numbers conveniently and present the data realistically with certainty to the extent possible. These ideas are discussed below in detail.

1.4.1 Scientific Notation

As chemistry is the study of atoms and molecules, which have extremely

low masses and are present in extremely large numbers, a chemist has to deal with numbers as large as 602, 200,000,000,000,000,000,000 for the molecules of 2 g of hydrogen gas or as small as 0.00000000000000000000000166 g mass of a H atom. Similarly, other constants such as Planck's constant, speed of light, charges on particles, etc., involve numbers of the above magnitude.

It may look funny for a moment to write or count numbers involving so many zeros but it offers a real challenge to do simple mathematical operations of addition, subtraction, multiplication or division with such numbers. You can write any two numbers of the above type and try any one of the operations you like to accept as a challenge, and then, you will really appreciate the difficulty in handling such numbers.

This problem is solved by using scientific notation for such numbers, i.e., exponential notation in which any number can be represented in the form $N \times 10^n$, where n is an exponent having positive or negative values and N is a number (called digit term) which varies between 1.000... and 9.999....

Thus, we can write 232.508 as 2.32508×10^2 in scientific notation. Note that while writing it, the decimal had to be moved to the left by two places and same is the exponent (2) of 10 in the scientific notation.

Similarly, 0.00016 can be written as 1.6×10^{-4}. Here, the decimal has to be moved four places to the right and (–4) is the exponent in the scientific notation.

While performing mathematical operations on numbers expressed in scientific notations, the following points are to be kept in mind.

Multiplication and Division

These two operations follow the same rules which are there for exponential numbers, i.e.

$$(5.6\times10^{5})\times(6.9\times10^{8})=(5.6\times6.9)(10^{5+8})$$
$$=(5.6\times6.9)\times10^{13}$$
$$=38.64\times10^{13}$$
$$=3.864\times10^{14}$$
$$(9.8\times10^{-2})\times(2.5\times10^{-6})=(9.8\times2.5)(10^{-2+(-6)})$$
$$=(9.8\times2.5)(10^{-2-6})$$
$$=24.50\times10^{-8}$$
$$=2.450\times10^{-7}$$
$$\frac{2.7\times10^{-3}}{5.5\times10^{4}}=(2.7\div5.5)(10^{-3-4})=0.4909\times10^{-7}$$
$$=4.909\times10^{-8}$$

Addition and Subtraction

For these two operations, first the numbers are written in such a way that they have the same exponent. After that, the coefficients (digit terms) are added or subtracted as the case
may be.

Thus, for adding 6.65×10^4 and 8.95×10^3, exponent is made same for both the numbers. Thus, we get $(6.65 \times 10^4) + (0.895 \times 10^4)$

Then, these numbers can be added as follows $(6.65 + 0.895) \times 10^4 = 7.545 \times 10^4$

Similarly, the subtraction of two numbers can be done as shown below:

$(2.5 \times 10^{-2}) - (4.8 \times 10^{-3})$

$= (2.5 \times 10^{-2}) - (0.48 \times 10^{-2})$

$= (2.5 - 0.48) \times 10^{-2} = 2.02 \times 10^{-2}$

1.4.2 Significant Figures

Every experimental measurement has some amount of uncertainty associated with it because of limitation of measuring instrument and the

skill of the person making the measurement. For example, mass of an object is obtained using a platform balance and it comes out to be 9.4g. On measuring the mass of this object on an analytical balance, the mass obtained is 9.4213g. The mass obtained by an analytical balance is slightly higher than the mass obtained by using a platform balance. Therefore, digit 4 placed after decimal in the measurement by platform balance is uncertain.

The uncertainty in the experimental or the calculated values is indicated by mentioning the number of significant figures. **Significant figures** are meaningful digits which are known with certainty plus one which is estimated or uncertain. The uncertainty is indicated by writing the certain digits and the last uncertain digit. Thus, if we write a result as 11.2 mL, we say the 11 is certain and 2 is uncertain and the uncertainty would be +1 in the last digit. Unless otherwise stated, an uncertainty of +1 in the last digit is always understood.

There are certain rules for determining the number of significant figures. These are stated below:

(1) All non-zero digits are significant. For example in 285 cm, there are three significant figures and in 0.25 mL, there are two significant figures.

(2) Zeros preceding to first non-zero digit are not significant. Such zero indicates the position of decimal point. Thus, 0.03 has one significant figure and 0.0052 has two significant figures.

(3) Zeros between two non-zero digits are significant. Thus, 2.005 has four significant figures.

(4) Zeros at the end or right of a number are significant, provided they are on the right side of the decimal point. For example, 0.200 g has three significant figures. But, if otherwise, the terminal zeros are not significant if there is no decimal point. For example, 100 has only one significant figure, but 100. has three significant figures and 100.0 has

four significant figures. Such numbers are better represented in scientific notation. We can express the number 100 as 1×10^2 for one significant figure, 1.0×10^2 for two significant figures and 1.00×10^2 for three significant figures.

(5) Counting the numbers of object, for example, 2 balls or 20 eggs, have infinite significant figures as these are exact numbers and can be represented by writing infinite number of zeros after placing a decimal i.e., 2 = 2.000000 or 20 = 20.000000.

In numbers written in scientific notation, all digits are significant e.g., 4.01×10^2 has three significant figures, and 8.256×10^{-3} has four significant figures.

However, one would always like the results to be precise and accurate. Precision and accuracy are often referred to while we talk about the measurement.

Precision refers to the closeness of various measurements for the same quantity. However, **accuracy** is the agreement of a particular value to the true value of the result. For example, if the true value for a result is 2.00 g and student 'A' takes two measurements and reports the results as 1.95 g and 1.93 g. These values are precise as they are close to each other but are not accurate. Another student 'B' repeats the experiment and obtains 1.94 g and 2.05 g as the results for two measurements. These observations are neither precise nor accurate. When the third student 'C' repeats these measurements and reports 2.01 g and 1.99 g as the result, these values are both precise and accurate. This can be more clearly understood from the data given in Table 1.4.

Table 1.4 Data to Illustrate Precision and Accuracy

Measurements/g			
	1	2	Average (g)
Student A	1.95	1.93	1.940
Student B	1.94	2.05	1.995
Student C	2.01	1.99	2.000

Addition and Subtraction of Significant Figures

The result cannot have more digits to the right of the decimal point than either of the original numbers.

12.11

18.0

1.012

31.122

Here, 18.0 has only one digit after the decimal point and the result should be reported only up to one digit after the decimal point, which is 31.1.

Multiplication and Division of Significant Figures

In these operations, the result must be reported with no more significant figures as in the measurement with the few significant figures.

$2.5 \times 1.25 = 3.125$

Since 2.5 has two significant figures, the result should not have more than two significant figures, thus, it is 3.1.

While limiting the result to the required number of significant figures as done in the above mathematical operation, one has to keep in mind the following points for rounding off the numbers

1. If the rightmost digit to be removed is more than 5, the preceding number is increased by one. For example, 1.386. If we have to remove 6, we have to round it to 1.39.
2. If the rightmost digit to be removed is less than 5, the preceding number is not changed. For example, 4.334 if 4 is to be removed, then the result is rounded upto 4.33.
3. If the rightmost digit to be removed is 5, then the preceding number

is not changed if it is an even number but it is increased by one if it is an odd number. For example, if 6.35 is to be rounded by removing 5, we have to increase 3 to 4 giving 6.4 as the result. However, if 6.25 is to be rounded off it is rounded off to 6.2.

1.4.3 Dimensional Analysis

Often while calculating, there is a need to convert units from one system to the other. The method used to accomplish this is called **factor label method** or **unit factor method** or **dimensional analysis**. This is illustrated below.

Example

A piece of metal is 3 inch (represented by in) long. What is its length in cm?

Solution

We know that 1 in = 2.54 cm

From this equivalence, we can write

$$\frac{1\text{ in}}{2.54\text{ cm}} = 1 = \frac{2.54\text{ cm}}{1\text{ in}}$$

Thus, $\frac{1\text{ in}}{2.54\text{ cm}}$ equals 1 and $\frac{2.54\text{ cm}}{1\text{ in}}$ also equals 1. Both of these are called **unit factors**. If some number is multiplied by these unit factors (i.e., 1), it will not be affected otherwise.

Say, the 3 in given above is multiplied by the unit factor. So,

3 in = 3 in × $\frac{2.54\text{ cm}}{1\text{ in}}$ = 3 × 2.54 cm = 7.62 cm

Now, the unit factor by which multiplication is to be done is that unit factor ($\frac{2.54\text{ cm}}{1\text{ in}}$ in the above case) which gives the desired units i.e., the numerator should have that part which is required in the desired result.

It should also be noted in the above example that units can be handled just like other numerical part. It can be cancelled, divided, multiplied, squared, etc. Let us study one more example.

Example

A jug contains 2L of milk. Calculate the volume of the milk in m^3.

Solution

Since 1 L = 1000 cm^3

and 1m = 100 cm, which gives $\frac{1\text{ m}}{100\text{ cm}} = 1 = \frac{100\text{ cm}}{1\text{ m}}$

To get m^3 from the above unit factors, the first unit factor is taken and it is cubed.

$$\left(\frac{1\text{ m}}{100\text{ cm}}\right)^3 \Rightarrow \frac{1\text{ m}^3}{10^6\text{ cm}^3} = (1)^3 = 1$$

Now 2 L = 2×1000 cm^3

The above is multiplied by the unit factor

$$2\times1000\text{ cm}^3 \times \frac{1\text{ m}^3}{10^6\text{ cm}^3} = \frac{2\text{ m}^3}{10^3} = 2\times10^{-3}\text{m}^3$$

Example

How many seconds are there in 2 days?

Solution

Here, we know 1 day = 24 hours (h)

or $\frac{1\text{day}}{24\text{ h}} = 1 = \frac{24\text{ h}}{1\text{day}}$

then, 1h = 60 min

or $\frac{1\text{ h}}{60\text{ min}} = 1 = \frac{60\text{ min}}{1\text{ h}}$

so, for converting 2 days to seconds,

i.e., 2 days – – – – – – = – – – seconds

The unit factors can be multiplied in series in one step only as follows:

$$2\text{ day}\times\frac{24\text{ h}}{1\text{day}}\times\frac{60\text{ min}}{1\text{ h}}\times\frac{60\text{ s}}{1\text{ min}}$$

= 2 × 24 × 60 × 60 s

= 172800 s

1.5 Laws of Chemical Combinations

The combination of elements to form compounds is governed by the following five basic laws.



Antoine Lavoisier

(1743–1794)

1.5.1 Law of Conservation of Mass

This law was put forth by Antoine Lavoisier in 1789. He performed careful experimental studies for combustion reactions and reached to the conclusion that in all physical and chemical changes, there is no net change in mass duting the process. Hence, he reached to the conclusion that matter can neither be created nor destroyed. This is called ‘Law of Conservation of Mass’. This law formed the basis for several later developments in chemistry. Infact, this was the result of exact measurement of masses of reactants and products, and carefully planned experiments performed by Lavoisier.



Joseph Proust

(1754–1826)

1.5.2 Law of Definite Proportions

This law was given by, a French chemist, Joseph Proust. He stated that a given compound always contains exactly the same proportion of elements by weight.

Proust worked with two samples of cupric carbonate — one of which was of natural origin and the other was synthetic. He found that the composition of elements present in it was same for both the samples as shown below:

	% of copper	% of carbon	% of oxygen
Natural Sample	51.35	9.74	38.91
Synthetic Sample	51.35	9.74	38.91

Thus, he concluded that irrespective of the source, a given compound always contains same elements combined together in the same proportion by mass. The validity of this law has been confirmed by various experiments. It is sometimes also referred to as **Law of Definite Composition**.

1.5.3 Law of Multiple Proportions

This law was proposed by Dalton in 1803. According to this law, if two elements can combine to form more than one compound, the masses of one element that combine with a fixed mass of the other element, are in the ratio of small whole numbers.

For example, hydrogen combines with oxygen to form two compounds, namely, water and hydrogen peroxide.

$$\underset{2g}{\text{Hydrogen}} + \underset{16g}{\text{Oxygen}} \rightarrow \underset{18g}{\text{Water}}$$

$$\underset{2g}{\text{Hydrogen}} + \underset{32g}{\text{Oxygen}} \rightarrow \underset{34g}{\text{Hydrogen Peroxide}}$$

Here, the masses of oxygen (i.e., 16 g and 32 g), which combine with a

fixed mass of hydrogen (2g) bear a simple ratio, i.e., 16:32 or 1: 2.



Joseph Louis

Gay Lussac

1.5.4 Gay Lussac's Law of Gaseous Volumes

This law was given by Gay Lussac in 1808. He observed that when gases combine or are produced in a chemical reaction they do so in a simple ratio by volume, provided all gases are at
the same temperature and pressure.

Thus, 100 mL of hydrogen combine with 50 mL of oxygen to give 100 mL of water vapour.

Hydrogen	+ Oxygen	→ Water
100 mL	50 mL	100 mL

Thus, the volumes of hydrogen and oxygen which combine (i.e., 100 mL and
50 mL) bear a simple ratio of 2:1.

Gay Lussac's discovery of integer ratio in volume relationship is actually the law of definite proportions by volume. The law of definite proportions, stated earlier, was with respect to mass. The Gay Lussac's law was explained properly by the work of Avogadro in 1811.

1.5.5 Avogadro's Law

In 1811, Avogadro proposed that equal volumes of all gases at the same temperature and pressure should contain equal number of molecules.

Avogadro made a distinction between **atoms** and **molecules** which is quite understandable in present times. If we consider again the reaction of hydrogen and oxygen to produce water, we see that two volumes of hydrogen combine with one volume of oxygen to give two volumes of water without leaving any unreacted oxygen.



Lorenzo Romano Amedeo Carlo Avogadro di Quareqa edi Carreto

(1776–1856)

Note that in the Fig. 1.9 (Page 16) each box contains equal number of molecules. In fact, Avogadro could explain the above result by considering the molecules to be **polyatomic.** If hydrogen and oxygen were considered as **diatomic** as recognised now, then the above results are easily understandable. However, Dalton and others believed at that time that atoms of the same kind cannot combine and molecules of oxygen or hydrogen containing two atoms did not exist. Avogadro's proposal was published in the French Journal de Physique. In spite of being correct, it did not gain much support.

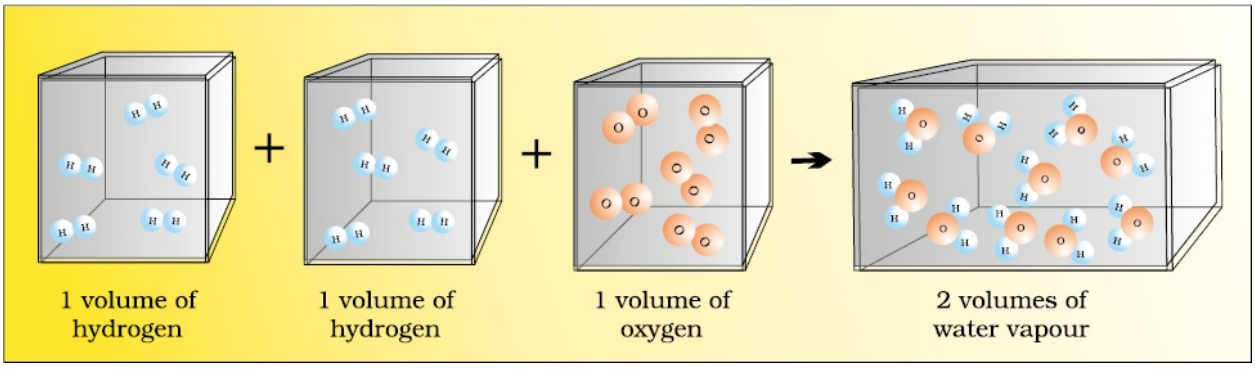


Fig. 1.9 Two volumes of hydrogen react with one volume of oxygen to give two volumes of water vapour

After about 50 years, in 1860, the first international conference on chemistry was held in Karlsruhe, Germany, to resolve various ideas. At the meeting, Stanislao Cannizaro presented a sketch of a course of chemical philosophy, which emphasised on the importance of Avogadro's work.



John Dalton

(1776–1884)

1.6 Dalton's Atomic Theory

Although the origin of the idea that matter is composed of small indivisible particles called 'a-tomio' (meaning, indivisible), dates back to the time of Democritus, a Greek Philosopher (460–370 BC), it again started emerging as a result of several experimental studies which led to the laws mentioned above.

In 1808, Dalton published 'A New System of Chemical Philosophy', in which he proposed the following :

1. Matter consists of indivisible atoms.
2. All atoms of a given element have identical properties, including identical mass. Atoms of different elements differ in mass.
3. Compounds are formed when atoms of different elements combine in a fixed ratio.

4. Chemical reactions involve reorganisation of atoms. These are neither created nor destroyed in a chemical reaction.

Dalton's theory could explain the laws of chemical combination. However, it could not explain the laws of gaseous volumes. It could not provide the reason for combining of atoms, which was answered later by other scientists.

1.7 Atomic and Molecular Masses

After having some idea about the terms atoms and molecules, it is appropriate here to understand what do we mean by atomic and molecular masses.

1.7.1 Atomic Mass

The atomic mass or the mass of an atom is actually very-very small because atoms are extremely small. Today, we have sophisticated techniques e.g., mass spectrometry for determining the atomic masses fairly accurately. But in the nineteenth century, scientists could determine the mass of one atom **relative** to another by experimental means, as has been mentioned earlier. Hydrogen, being the lightest atom was arbitrarily assigned a mass of 1 (without any units) and other elements were assigned masses relative to it. However, the present system of atomic masses is based on carbon-12 as the standard and has been agreed upon in 1961. Here, Carbon-12 is one of the **isotopes** of carbon and can be represented as 12C. In this system, 12C is assigned a mass of exactly 12 atomic mass unit (**amu**) and masses of all other atoms are given relative to this standard. One **atomic mass unit** is defined as a mass exactly equal to one-twelfth of the mass of one carbon - 12 atom.

And 1 amu = 1.66056×10–24 g

Mass of an atom of hydrogen = 1.6736×10–24 g

Thus, in terms of amu, the mass

of hydrogen atom = $\frac{1.6736 \times 10^{-24}\,\text{g}}{1.66056 \times 10^{-24}\,\text{g}}$

= 1.0078 amu

= 1.0080 amu

Similarly, the mass of oxygen - 16 (16O) atom would be 15.995 amu.

At present, **'amu'** has been replaced by **'u'**, which is known as **unified mass**.

When we use atomic masses of elements in calculations, we actually use average atomic masses of elements, which are explained below.

1.7.2 Average Atomic Mass

Many naturally occurring elements exist as more than one isotope. When we take into account the existence of these isotopes and their relative abundance (per cent occurrence), the average atomic mass of that element can be computed. For example, carbon has the following three isotopes with relative abundances and masses as shown against each of them.

Isotope	Relative Abundance (%)	Atomic Mass (amu)
^{12}C	98.892	12
^{13}C	1.108	13.00335
^{14}C	2×10^{-10}	14.00317

From the above data, the average atomic mass of carbon will come out to be:

(0.98892) (12 u) + (0.01108) (13.00335 u) + (2 × 10–12) (14.00317 u) = 12.011 u

Similarly, average atomic masses for other elements can be calculated. In the periodic table of elements, the atomic masses mentioned for different elements actually represent their average atomic masses.

1.7.3 Molecular Mass

Molecular mass is the sum of atomic masses of the elements present in a molecule. It is obtained by multiplying the atomic mass of each element by the number of its atoms and adding them together. For example,

molecular mass of methane, which contains one carbon atom and four hydrogen atoms, can be obtained as follows:

Molecular mass of methane,

(CH_4) = (12.011 u) + 4 (1.008 u)

= 16.043 u

Similarly, molecular mass of water (H_2O)

= 2 × atomic mass of hydrogen + 1 × atomic mass of oxygen

= 2 (1.008 u) + 16.00 u

= 18.02 u

1.7.4 Formula Mass

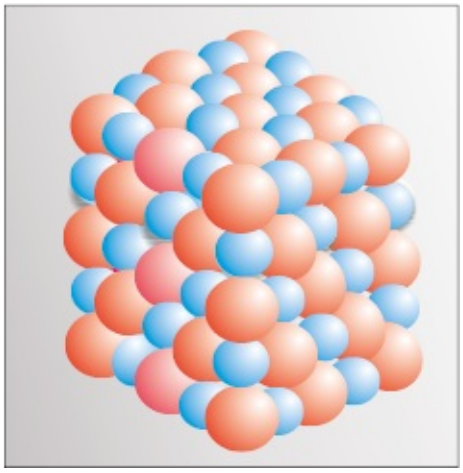


Fig. 1.10 Packing of Na+ and Cl– ions in sodium chloride

Some substances, such as sodium chloride, do not contain discrete molecules as their constituent units. In such compounds, positive (sodium ion) and negative (chloride ion) entities are arranged in a three-dimensional structure, as shown in Fig. 1.10.

It may be noted that in sodium chloride, one Na+ ion is surrounded by six Cl– ion and vice-versa.

The formula, such as NaCl, is used to calculate the **formula mass** instead of molecular mass as in the solid state sodium chloride does not exist as a single entity.

Thus, the formula mass of sodium chloride is atomic mass of sodium +

atomic mass of chlorine

= 23.0 u + 35.5 u = 58.5 u

Problem 1.1

Calculate the molecular mass of glucose ($C_6H_{12}O_6$) molecule.

Solution

Molecular mass of glucose ($C_6H_{12}O_6$)

= 6(12.011 u) + 12(1.008 u) + 6(16.00 u)

= (72.066 u) + (12.096 u) + (96.00 u)

= 180.162 u

1.8 Mole concept and Molar Masses

Atoms and molecules are extremely small in size and their numbers in even a small amount of any substance is really very large. To handle such large numbers, a unit of convenient magnitude is required.

Just as we denote one dozen for 12 items, score for 20 items, gross for 144 items, we use the idea of mole to count entities at the microscopic level (i.e., atoms, molecules, particles, electrons, ions, etc).

In SI system, **mole** (symbol, mol) was introduced as seventh base quantity for the amount of a substance.

One mole is the amount of a substance that contains as many particles or entities as there are atoms in exactly 12 g (or 0.012 kg) of the 12**C isotope.** It may be emphasised that the mole of a substance always

contains the same number of entities, no matter what the substance may be. In order to determine this number precisely, the mass of a carbon–12 atom was determined by a mass spectrometer and found to be equal to 1.992648 × 10–23 g. Knowing that one mole of carbon weighs 12 g, the number of atoms in it is equal to:

$$\frac{12\,\text{g/mol}\ ^{12}\text{C}}{1.992648\times10^{-23}\,\text{g}/^{12}\,\text{C atom}}$$
$$= 6.0221367\times10^{23}\ \text{atoms/mol}$$

This number of entities in 1 mol is so important that it is given a separate name and symbol. It is known as **'Avogadro constant'**, or Avogadro number denoted by N_A in honour of Amedeo Avogadro. To appreciate the largeness of this number, let us write it with all zeroes without using any powers of ten.

602213670000000000000000

Hence, so many entities (atoms, molecules or any other particle) constitute one mole of a particular substance.

We can, therefore, say that 1 mol of hydrogen atoms = 6.022×1023 atoms

1 mol of water molecules = 6.022×1023 water molecules

1 mol of sodium chloride = 6.022 × 1023 formula units of sodium chloride

Having defined the mole, it is easier to know the mass of one mole of a substance or the constituent entities. **The mass of one mole of a substance in grams is called its molar mass.** The molar mass in grams is numerically equal to atomic/molecular/formula mass in u.

Molar mass of water = 18.02 g mol-1

Molar mass of sodium chloride = 58.5 g mol-1

1.9 Percentage Composition

So far, we were dealing with the number of entities present in a given sample. But many a time, information regarding the percentage of a particular element present in a compound is required. Suppose, an unknown or new compound is given to you, the first question you would ask is: what is its formula or what are its constituents and in what ratio are they present in the given compound? For known compounds also, such information provides a check whether the given sample contains the

same percentage of elements as present in a pure sample. In other words, one can check the purity of a given sample by analysing this data.



Fig. 1.11 One mole of various substances

Let us understand it by taking the example of water (H_2O). Since water contains hydrogen and oxygen, the percentage composition of both these elements can be calculated as follows:

Mass % of an element =

$$\frac{\text{mass of that element in the compound} \times 100}{\text{molar mass of the compound}}$$

$$\text{Molar mass of water} = 18.02\ \text{g}$$

$$\text{Mass \% of hydrogen} = \frac{2\times1.008}{18.02}\times100 = 11.18$$

$$\text{Mass \% of oxygen} = \frac{16.00}{18.02}\times100 = 88.79$$

Let us take one more example. What is the percentage of carbon, hydrogen and oxygen in ethanol?

Molecular formula of ethanol is: C_2H_5OH Molar mass of ethanol is:

$(2\times12.01 + 6\times1.008 + 16.00)\ \text{g} = 46.068\ \text{g}$

Mass per cent of carbon = $= \frac{24.02\,g}{46.068\,g} \times 100$ = 52.14%

Mass per cent of hydrogen = $= \frac{6.048\,g}{46.068\,g} \times 100$ = 13.13%

Mass per cent of oxygen = $= \frac{16.00\,g}{46.068\,g} \times 100$ = 34.73%

After understanding the calculation of
per cent of mass, let us now see what information can be obtained from the
per cent composition data.

1.9.1 Empirical Formula for Molecular Formula

An **empirical formula** represents the simplest whole number ratio of various atoms present in a compound, whereas, the **molecular formula** shows the exact number of different types of atoms present in a molecule of a compound.

If the mass per cent of various elements present in a compound is known, its empirical formula can be determined. Molecular formula can further be obtained if the molar mass is known. The following example illustrates this sequence.

Problem 1.2

A compound contains 4.07% hydrogen, 24.27% carbon and 71.65% chlorine. Its molar mass is 98.96 g. What are its empirical and molecular formulas?

Solution

Step 1. Conversion of mass per cent to grams

Since we are having mass per cent, it is convenient to use 100 g of the compound as the starting material. Thus, in the
100 g sample of the above compound, 4.07g hydrogen, 24.27g carbon and 71.65g chlorine are present.

Step 2. Convert into number moles of each element

Divide the masses obtained above by respective atomic masses of various elements. This gives the number of moles of constituent elements in the compound

Moles of hydrogen = $\frac{4.07\,g}{1.008\,g}$ = 4.04

Moles of carbon = $\frac{24.27\,g}{12.01\,g} = 2.021$

Moles of chlorine = $\frac{71.65\,g}{35.453\,g} = 2.021$

Step 3. Divide each of the mole values obtained above by the smallest number amongst them

Since 2.021 is smallest value, division by it gives a ratio of 2:1:1 for H:C:Cl .

In case the ratios are not whole numbers, then they may be converted into whole number by multiplying by the suitable coefficient.

Step 4. Write down the empirical formula by mentioning the numbers after writing the symbols of respective elements

CH_2Cl is, thus, the empirical formula of the above compound.

Step 5. Writing molecular formula

(a) Determine empirical formula mass by

adding the atomic masses of various atoms present in the empirical formula.

For CH_2Cl, empirical formula mass is

12.01 + (2 × 1.008) + 35.453

= 49.48 g

(b) Divide Molar mass by empirical formula mass

$$\frac{\text{Molar mass}}{\text{Empirical formula mass}} = \frac{98.96\,g}{49.48\,g}$$

= 2 = (n)

(c) Multiply empirical formula by n obtained above to get the molecular formula

Empirical formula = CH_2Cl, n = 2. Hence molecular formula is $C_2H_4Cl_2$.

1.10 Stoichiometry and Stoichiometric Calculations

The word ‘stoichiometry’ is derived from two Greek words — stoicheion (meaning, element) and metron (meaning, measure). Stoichiometry, thus, deals with the calculation of masses (sometimes volumes also) of the reactants and the products involved in a chemical reaction. Before understanding how to calculate the amounts of reactants required or the products produced in a chemical reaction, let us study what information is available from the **balanced** chemical equation of a given reaction. Let us consider the combustion of methane. A balanced equation for this reaction is as given below:

CH_4 (g) + $2O_2$ (g) → CO_2 (g) + 2 H_2O (g)

Here, methane and dioxygen are called reactants and carbon dioxide and water are called products. Note that all the reactants and the products are gases in the above reaction and this has been indicated by letter (g) in the brackets next to its formula. Similarly, in case of solids and liquids, (s) and (l) are written respectively.

The coefficients 2 for O_2 and H_2O are called stoichiometric coefficients. Similarly the coefficient for CH_4 and CO_2 is one in each case. They represent the number of molecules (and moles as well) taking part in the reaction or formed in the reaction.

Thus, according to the above chemical reaction,

• One **mole** of CH_4(g) reacts with two **moles** of O_2(g) to give one **mole** of CO_2(g) and two **moles** of H_2O(g)

• One **molecule** of CH_4(g) reacts with

2 **molecules** of O_2(g) to give one **molecule** of CO_2(g) and 2 molecules of H_2O(g)

• 22.7 L of CH_4(g) reacts with 45.4 L of O_2 (g) to give 22.7 L of CO_2 (g) and 45.4 L of H_2O(g)

• 16 g of CH_4 (g) reacts with 2×32 g of O_2 (g) to give 44 g of CO_2 (g) and 2×18 g of H_2O (g).

From these relationships, the given data can be interconverted as follows:

$$\text{mass} \leftrightharpoons \text{moles} \leftrightharpoons \text{no. of molecules}$$

$$\frac{\text{Mass}}{\text{Volume}} = \text{Density}$$

1.10.1 Limiting Reagent

Many a time, reactions are carried out with the amounts of reactants that are different than the amounts as required by a balanced chemical reaction. In such situations, one reactant is in more amount than the amount required by balanced chemical reaction. The reactant which is present in the least amount gets consumed after sometime and after that further reaction does not take place whatever be the amount of the other reactant. Hence, the reactant, which gets consumed first, limits the amount of product formed and is, therefore, called the **limiting reagent**.

In performing stoichiometric calculations, this aspect is also to be kept in mind.

1.10.2 Reactions in Solutions

A majority of reactions in the laboratories are carried out in solutions. Therefore, it is important to understand as how the amount of substance is expressed when it is present in the solution. The concentration of a solution or the amount of substance present in its given volume can be expressed in any of the following ways.

1. Mass per cent or weight per cent (w/w %)
2. Mole fraction
3. Molarity
4. Molality

Let us now study each one of them in detail.

Balancing a chemical equation

According to the law of conservation of mass, a balanced chemical equation has the same number of atoms of each element on both sides of the equation. Many chemical equations can be balanced by trial and error. Let us take the reactions of a few metals and non-metals with oxygen to give oxides

$4\ Fe(s) + 3O_2(g) \rightarrow 2Fe_2O_3(s)$ (a) balanced equation

$2\ Mg(s) + O_2(g) \rightarrow 2MgO(s)$ (b) balanced equation

$P_4(s) + O_2\ (g) \rightarrow P_4O_{10}(s)$ (c) unbalanced equation

Equations (a) and (b) are balanced, since there are same number of metal and oxygen atoms on each side of the equations. However equation (c) is not balanced. In this equation, phosphorus atoms are balanced but not the oxygen atoms. To balance it, we must place the coefficient 5 on the left of oxygen on the left side of the equation to balance the oxygen atoms appearing on the right side of the equation.

$P_4(s) + 5O_2(g) \rightarrow P_4O_{10}(s)$ balanced equation

Now, let us take combustion of propane, C_3H_8. This equation can be balanced in steps.

Step 1 Write down the correct formulas of reactants and products. Here, propane and oxygen are reactants, and carbon dioxide and water are products.

$C_3H_8(g) + O_2(g) \rightarrow CO_2\ (g) + H_2O(l)$ unbalanced equation

Step 2 Balance the number of C atoms: Since 3 carbon atoms are in the reactant, therefore, three CO_2 molecules are required on the right side.

$C_3H_8\ (g) + O_2\ (g) \rightarrow 3CO_2\ (g) + H_2O\ (l)$

Step 3 Balance the number of H atoms: on the left there are 8 hydrogen atoms in the reactants however, each molecule of water has two hydrogen atoms, so four molecules of water will be required for eight hydrogen atoms on the right side.

$C_3H_8\ (g) + O_2\ (g) \rightarrow 3CO_2\ (g) + 4H_2O\ (l)$

Step 4 Balance the number of O atoms: There are 10 oxygen atoms on the right side ($3 \times 2 = 6$ in CO_2 and $4 \times 1 = 4$ in water). Therefore, five O_2 molecules are needed to supply the

required 10 CO_2 and 4 × 1= 4 in water). Therefore, five O_2 molecules are needed to supply the required 10 oxygen atoms.

C_3H_8 (g) +5O_2 (g) → 3CO_2 (g) + 4H_2O (l)

Step 5 Verify that the number of atoms of each element is balanced in the final equation. The equation shows three carbon atoms, eight hydrogen atoms, and 10 oxygen atoms on each side.

All equations that have correct formulas for all reactants and products can be balanced. Always remember that subscripts in formulas of reactants and products cannot be changed to balance an equation.

Problem 1.3

Calculate the amount of water (g) produced by the combustion of 16 g of methane.

Solution

The balanced equation for the combustion of methane is :

CH_4 (g) + 2O_2 (g) ® CO_2 (g) + 2H_2O (g)

(i) 16 g of CH_4 corresponds to one mole.

(ii) From the above equation, 1 mol of CH_4 (g) gives 2 mol of H_2O (g).

2 mol of water (H_2O) = 2 × (2+16)

= 2 × 18 = 36 g

1 mol H_2O = 18 g H_2O ⇒ $\frac{18\ g\ H_2O}{1\ mol\ H_2O}$ = 1

Hence, 2 mol H_2O × $\frac{18\ g\ H_2O}{1\ mol\ H_2O}$

= 2 × 18 g H_2O = 36 g H_2O

Problem 1.4

How many moles of methane are required to produce 22g CO_2 (g) after combustion?

Solution

According to the chemical equation,

CH_4 (g) + $2O_2$ (g) ® CO_2 (g) + $2H_2O$ (g)

44g CO_2 (g) is obtained from 16 g CH_4 (g).

[∴1 mol CO_2(g) is obtained from 1 mol of CH_4(g)]

Number of moles of CO_2 (g)

$$= 22\ g\ CO_2\ (g) \times \frac{1\ mol\ CO_2\ (g)}{44\ g\ CO_2\ (g)}$$

= 0.5 mol CO_2 (g)

Hence, 0.5 mol CO_2 (g) would be obtained from 0.5 mol CH_4 (g) or 0.5 mol of CH_4 (g) would be required to produce 22 g CO_2 (g).

Problem 1.5

50.0 kg of N_2 (g) and 10.0 kg of H_2 (g) are mixed to produce NH_3 (g). Calculate the amount of NH_3 (g) formed. Identify the limiting reagent in the production of NH_3 in this situation.

Solution

A balanced equation for the above reaction is written as follows :

$$N_2\ (g) + 3H_2\ (g) \rightleftharpoons 2\ NH_3\ (g)$$

Calculation of moles :

Number of moles of N_2

$$= 50.0\ kg\ N_2 \times \frac{1000\ g\ N_2}{1\ kg\ N_2} \times \frac{1\ mol\ N_2}{28.0\ g\ N_2}$$

$$= 17.86 \times 10^2\ mol$$

Number of moles of H_2

$$= 10.00\ kg\ H_2 \times \frac{1000\ g\ H_2}{1\ kg\ H_2} \times \frac{1\ mol\ H_2}{2.016\ g\ H_2}$$

= 4.96×103 mol

According to the above equation, 1 mol N_2 (g) requires 3 mol H_2 (g), for the reaction. Hence, for 17.86×102 mol of N_2, the moles of H_2 (g) required would be

$$17.86\times10^{2}\ \text{mol}\,N_2\times\frac{3\ \text{mol}\,H_2\,(g)}{1\ \text{mol}\,N_2\,(g)}$$

= 5.36 ×103 mol H_2

But we have only 4.96×103 mol H_2. Hence, dihydrogen is the limiting reagent in this case. So, $NH_3(g)$ would be formed only from that amount of available dihydrogen i.e., 4.96 × 103 mol

Since 3 mol $H_2(g)$ gives 2 mol $NH_3(g)$

4.96×103 mol H_2 (g) × $\frac{2\ \text{mol}\,NH_3\ (g)}{3\ \text{mol}\,H_2\ (g)}$

= 3.30×103 mol NH_3 (g)

3.30×103 mol NH_3 (g) is obtained.

If they are to be converted to grams, it is done as follows :

1 mol NH_3 (g) = 17.0 g NH_3 (g)

3.30×103 mol NH_3 (g) × $\frac{17.0\ \text{g}\,NH_3\ (g)}{1\ \text{mol}\,NH_3\ (g)}$

= 3.30×103×17 g NH_3 (g)

= 56.1×103 g NH_3

= 56.1 kg NH_3

1. Mass per cent

It is obtained by using the following relation:

$$\text{Mass per cent} = \frac{\text{Mass of solute}}{\text{Mass of solution}}\times100$$

Problem 1.6

A solution is prepared by adding 2 g of a substance A to 18 g of water. Calculate the mass per cent of the solute.

Solution

$$\text{Mass per cent of A} = \frac{\text{Mass of A}}{\text{Mass of solution}} \times 100$$

$$= \frac{2\,\text{g}}{2\,\text{g of A} + 18\,\text{g of water}} \times 100$$

$$= \frac{2\,\text{g}}{20\,\text{g}} \times 100$$

$$= 10\%$$

2. Mole Fraction

It is the ratio of number of moles of a particular component to the total number of moles of the solution. If a substance 'A' dissolves in substance 'B' and their number of moles are n_A and n_B, respectively, then the mole fractions of A and B are given as:

$$\text{Mole fraction of A} = \frac{\text{No. of moles of A}}{\text{No. of moles of solutions}}$$

$$= \frac{n_A}{n_A + n_B}$$

$$\text{Mole fraction of B} = \frac{\text{No. of moles of B}}{\text{No. of moles of solutions}}$$

$$= \frac{n_B}{n_A + n_B}$$

3. Molarity

It is the most widely used unit and is denoted by M. It is defined as the number of moles of the solute in 1 litre of the solution. Thus,

$$\text{Molarity (M)} = \frac{\text{No. of moles of solute}}{\text{Volume of solution in litres}}$$

Suppose, we have 1 M solution of a substance, say NaOH, and we want

to prepare a 0.2 M solution from it.

1 M NaOH means 1 mol of NaOH present in 1 litre of the solution. For 0.2 M solution, we require 0.2 moles of NaOH dissolved in

1 litre solution.

Hence, for making 0.2M solution from 1M solution, we have to take that volume of 1M NaOH solution, which contains 0.2 mol of NaOH and dilute the solution with water to 1 litre.

Now, how much volume of concentrated (1M) NaOH solution be taken, which contains 0.2 moles of NaOH can be calculated as follows:

If 1 mol is present in 1L or 1000 mL solution

then, 0.2 mol is present in $\frac{1000\,\text{mL}}{1\,\text{mol}} \times 0.2\,\text{mol solution}$

= 200 mL solution

Thus, 200 mL of 1M NaOH are taken and enough water is added to dilute it to make it 1 litre.

In fact for such calculations, a general formula, $M_1 \times V_1 = M_2 \times V_2$ where M and V are molarity and volume, respectively, can be used. In this case, M_1 is equal to 0.2M; V_1 = 1000 mL and, M_2 = 1.0M; V_2 is to be calculated.

Substituting the values in the formula:

0.2 M × 1000 mL = 1.0 M × V_2

$$\therefore V_2 = \frac{0.2\,\text{M} \times 1000\,\text{mL}}{1.0\,\text{M}} = 200\,\text{L}$$

Note that the **number of moles of solute** (NaOH) was 0.2 in 200 mL and it has remained the same, i.e., 0.2 even after dilution (in 1000 mL) as we have changed just the amount of solvent (i.e., water) and have not done anything with respect to NaOH. But keep in mind the concentration.

Problem 1.7

Calculate the molarity of NaOH in the solution prepared by dissolving its 4 g in enough water to form 250 mL of the solution.

Solution

Since molarity (M)

$$= \frac{\text{No. of moles of solute}}{\text{Volume of solution in litres}}$$

$$= \frac{\text{Mass of NaOH / Molar mass of NaOH}}{0.250\,\text{L}}$$

$$= \frac{4\,\text{g}/40\,\text{g}}{0.250\,\text{L}} = \frac{0.1\,\text{mol}}{0.250\,\text{L}}$$

$$= 0.4\,\text{mol}^{-1}$$

$$= 0.4\,\text{M}$$

Note that molarity of a solution depends upon temperature because volume of a solution is temperature dependent.

4. Molality

It is defined as the number of moles of solute present in 1 kg of solvent. It is denoted by m.

$$\text{Thus, Molality (m)} = \frac{\text{No. of moles of solute}}{\text{Mass of solvent in kg}}$$

Problem 1.8

The density of 3 M solution of NaCl is

1.25 g mL–1. Calculate the molality of the solution.

Solution

M = 3 mol L–1

Mass of NaCl

in 1 L solution = 3 × 58.5 = 175.5 g

Mass of

1L solution = 1000 × 1.25 = 1250 g

(since density = 1.25 g mL^{-1})

Mass of water in solution = 1250 –75.5 = 1074.5 g

$$\text{Molality} = \frac{\text{No. of moles of solute}}{\text{Mass of solvent in kg}}$$

$$= \frac{3\ \text{mol}}{1.0745\,\text{kg}} = 2.79\ \text{m}$$

Often in a chemistry laboratory, a solution of a desired concentration is prepared by diluting a solution of known higher concentration. The solution of higher concentration is also known as stock solution. Note that the molality of a solution does not change with temperature since mass remains unaffected with temperature.

Summary

Chemistry, as we understand it today is not a very old discipline. People in ancient India, already had the knowledge of many scientific phenomenon much before the advent of modern science. They applied the knowledge in various walks of life.

The study of chemistry is very important as its domain encompasses every sphere of life. Chemists study the properties and structure of substances and the changes undergone by them. All substances contain matter, which can exist in three states – solid, liquid or gas. The constituent particles are held in different ways in these states of matter and they exhibit their characteristic properties. Matter can also be classified into elements, compounds or mixtures. An **element** contains particles of only one type, which may be **atoms** or **molecules**. The compounds are formed where atoms of two or more elements combine in a fixed ratio to each other. Mixtures occur widely and many of the substances present around us are mixtures.

When the properties of a substance are studied, measurement is inherent. The quantification of properties requires a system of measurement and units in which the quantities are to be expressed. Many systems of measurement exist, of which the English and the Metric Systems are widely used. The scientific community, however, has agreed to have a uniform and common system throughout the world, which is abbreviated as SI units (International System of Units).

Since measurements involve recording of data, which are always associated with a certain amount of uncertainty, the proper handling of data obtained by measuring the quantities is very

important. The measurements of quantities in chemistry are spread over a wide range of 10^{-31} to 10^{+23}. Hence, a convenient system of expressing the numbers in **scientific notation** is used. The uncertainty is taken care of by specifying the number of **significant figures,** in which the observations are reported. The **dimensional analysis** helps to express the measured quantities in different systems of units. Hence, it is possible to interconvert the results from one system of units to another.

The combination of different atoms is governed by basic laws of chemical combination — these being the **Law of Conservation of Mass, Law of Definite Proportions, Law of Multiple Proportions, Gay Lussac's Law of Gaseous Volumes** and **Avogadro Law**. All these laws led to the **Dalton's atomic theory,** which states that atoms are building blocks of matter. The **atomic mass** of an element is expressed relative to ^{12}C isotope of carbon, which has an exact value of 12u. Usually, the atomic mass used for an element is the **average atomic mass** obtained by taking into account the natural abundance of different isotopes of that element. The **molecular mass** of a molecule is obtained by taking sum of the atomic masses of different atoms present in a molecule. The **molecular formula** can be calculated by determining the mass per cent of different elements present in a compound and its molecular mass.

The number of atoms, molecules or any other particles present in a given system are expressed in the terms of **Avogadro constant** (6.022×10^{23}). This is known as **1 mol** of the respective particles or entities.

Chemical reactions represent the chemical changes undergone by different elements and compounds. A **balanced** chemical equation provides a lot of information. The coefficients indicate the molar ratios and the respective number of particles taking part in a particular reaction. The quantitative study of the reactants required or the products formed is called **stoichiometry**. Using stoichiometric calculations, the amount of one or more reactant(s) required to produce a particular amount of product can be determined and vice-versa. The amount of substance present in a given volume of a solution is expressed in number of ways, e.g., mass per cent, mole fraction, molarity and molality.

EXERCISES

1.1 Calculate the molar mass of the following:
(i) H_2O (ii) CO_2 (iii) CH_4

1.2 Calculate the mass per cent of different elements present in sodium sulphate (Na_2SO_4).

1.3 Determine the empirical formula of an oxide of iron, which has 69.9% iron and 30.1% dioxygen by mass.

1.4 Calculate the amount of carbon dioxide that could be produced when
(i) 1 mole of carbon is burnt in air.
(ii) 1 mole of carbon is burnt in 16 g of dioxygen.
(iii) 2 moles of carbon are burnt in 16 g of dioxygen.

1.5 Calculate the mass of sodium acetate (CH_3COONa) required to make 500 mL of 0.375 molar aqueous solution. Molar mass of sodium acetate is 82.0245 g mol^{-1}.

1.6 Calculate the concentration of nitric acid in moles per litre in a sample which has a density, 1.41 g mL^{-1} and the mass per cent of nitric acid in it being 69%.

1.7 How much copper can be obtained from 100 g of copper sulphate ($CuSO_4$)?

1.8 Determine the molecular formula of an oxide of iron, in which the mass per cent of iron and oxygen are 69.9 and 30.1, respectively.

1.9 Calculate the atomic mass (average) of chlorine using the following data:

	% Natural Abundance	Molar Mass
^{35}Cl	75.77	34.9689
^{37}Cl	24.23	36.9659

1.10 In three moles of ethane (C_2H_6), calculate the following:

(i) Number of moles of carbon atoms.

(ii) Number of moles of hydrogen atoms.
(iii) Number of molecules of ethane.

1.11 What is the concentration of sugar ($C_{12}H_{22}O_{11}$) in mol L^{-1} if its 20 g are dissolved in enough water to make a final volume up to 2L?

1.12 If the density of methanol is 0.793 kg L^{-1}, what is its volume needed for making 2.5 L of its 0.25 M solution?

1.13 Pressure is determined as force per unit area of the surface. The SI unit of pressure, pascal is as shown below:

1Pa = 1N m^{-2}

If mass of air at sea level is 1034 g cm^{-2}, calculate the pressure in pascal.

1.14 What is the SI unit of mass? How is it defined?

1.15 Match the following prefixes with their multiples:

Prefixes Multiples

(i) micro 10^{6}

(ii) deca 10^{9}

(iii) mega 10^{-6}

(iv) giga 10^{-15}

(v) femto 10

1.16 What do you mean by significant figures?

1.17 A sample of drinking water was found to be severely contaminated with chloroform, $CHCl_3$, supposed to be carcinogenic in nature. The level of contamination was 15 ppm (by mass).

(i) Express this in per cent by mass.

(ii) Determine the molality of chloroform in the water sample.

1.18 Express the following in the scientific notation:

(i) 0.0048

(ii) 234,000

(iii) 8008

(iv) 500.0

(v) 6.0012

1.19 How many significant figures are present in the following?

(i) 0.0025

(ii) 208

(iii) 5005

(iv) 126,000

(v) 500.0

(vi) 2.0034

1.20 Round up the following upto three significant figures:

(i) 34.216

(ii) 10.4107

(iii) 0.04597

(iv) 2808

1.21 The following data are obtained when dinitrogen and dioxygen react together to form different compounds:

	Mass of dinitrogen	Mass of dioxygen
(i)	14 g	16 g
(ii)	14 g	32 g
(iii)	28 g	32 g
(iv)	28 g	80 g

(a) Which law of chemical combination is obeyed by the above experimental data? Give its statement.

(b) Fill in the blanks in the following conversions:

(i) 1 km = ... mm = ... pm

(ii) 1 mg = ... kg = ... ng

(iii) 1 mL = ... L = ... dm^3

1.22 If the speed of light is 3.0×10^8 m s^{-1}, calculate the distance

covered by light in
2.00 ns.
1.23 In a reaction
$A + B_2 \rightarrow AB_2$
Identify the limiting reagent, if any, in the following reaction mixtures.
(i) 300 atoms of A + 200 molecules of B
(ii) 2 mol A + 3 mol B
(iii) 100 atoms of A + 100 molecules of B
(iv) 5 mol A + 2.5 mol B
(v) 2.5 mol A + 5 mol B
1.24 Dinitrogen and dihydrogen react with each other to produce ammonia according to the following chemical equation:
$N_2(g) + H_2(g) \rightarrow 2NH_3(g)$
(i) Calculate the mass of ammonia produced if 2.00×10^3 g dinitrogen reacts with 1.00×10^3 g of dihydrogen.
(ii) Will any of the two reactants remain unreacted?
(iii) If yes, which one and what would be its mass?
1.25 How are 0.50 mol Na_2CO_3 and 0.50 M Na_2CO_3 different?
1.26 If 10 volumes of dihydrogen gas reacts with five volumes of dioxygen gas, how many volumes of water vapour would be produced?
1.27 Convert the following into basic units:
(i) 28.7 pm
(ii) 15.15 pm
(iii) 25365 mg
1.28 Which one of the following will have the largest number of atoms?
(i) 1 g Au (s)
(ii) 1 g Na (s)
(iii) 1 g Li (s)

(iv) 1 g of $Cl_2(g)$

1.29 Calculate the molarity of a solution of ethanol in water, in which the mole fraction of ethanol is 0.040 (assume the density of water to be one).

1.30 What will be the mass of one ^{12}C atom in g?

1.31 How many significant figures should be present in the answer of the following calculations?

(i) $\frac{0.02856 \times 298.15 \times 0.112}{0.5785}$

(ii) 5 × 5.364

(iii) 0.0125 + 0.7864 + 0.0215

1.32 Use the data given in the following table to calculate the molar mass of naturally occuring argon isotopes:

Isotope	Isotopic molar mass	Abundance
^{36}Ar	35.96755 g mol^{-1}	0.337%
^{38}Ar	37.96272 g mol^{-1}	0.063%
^{40}Ar	39.9624 g mol^{-1}	99.600%

1.33 Calculate the number of atoms in each of the following (i) 52 moles of Ar (ii) 52 u of He (iii) 52 g of He.

1.34 A welding fuel gas contains carbon and hydrogen only. Burning a small sample of it in oxygen gives 3.38 g carbon dioxide, 0.690 g of water and no other products. A volume of 10.0 L (measured at STP) of this welding gas is found to weigh 11.6 g. Calculate (i) empirical formula, (ii) molar mass of the gas, and (iii) molecular formula.

1.35 Calcium carbonate reacts with aqueous HCl to give $CaCl_2$ and CO_2 according to the reaction, $CaCO_3$ (s) + 2 HCl (aq) → $CaCl_2$ (aq) + $CO_2(g)$ + $H_2O(l)$

What mass of $CaCO_3$ is required to react completely with 25 mL of 0.75 M HCl?

1.36 Chlorine is prepared in the laboratory by treating manganese dioxide (MnO_2) with aqueous hydrochloric acid according to the reaction

$4\ HCl\ (aq) + MnO_2(s) \rightarrow 2H_2O\ (l) + MnCl_2(aq) + Cl_2\ (g)$

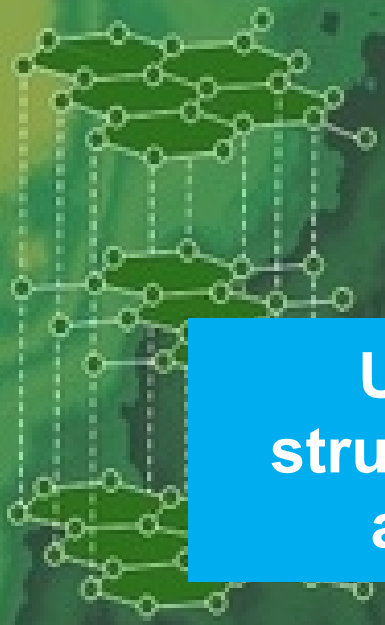
How many grams of HCl react with 5.0 g of manganese dioxide?

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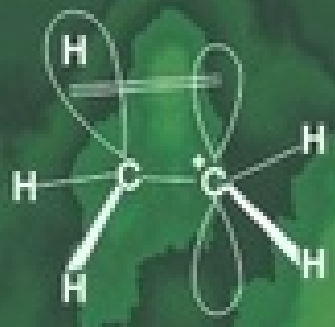
Textbook for Class XI



Unit 2
structure of atom

Chemistry

Part I



11082CH02

Unit 2

structure of atom

Objectives

After studying this unit you will be able to

- know about the discovery of electron, proton and neutron and their characteristics;
- describe Thomson, Rutherford and Bohr atomic models;
- understand the important features of the quantum mechanical model of atom;
- understand nature of electromagnetic radiation and Planck's quantum theory;
- explain the photoelectric effect and describe features of atomic spectra;
- state the de Broglie relation and Heisenberg uncertainty principle;
- define an atomic orbital in terms of quantum numbers;
- state aufbau principle, Pauli exclusion principle and Hund's rule of maximum multiplicity; and
- write the electronic configurations of atoms.

"The rich diversity of chemical behaviour of different elements can be traced to the differences in the internal structure of atoms of these elements".

The existence of atoms has been proposed since the time of early Indian and Greek philosophers (400 B.C.) who were of the view that atoms are the fundamental building blocks of matter. According to them, the continued subdivisions of matter would ultimately yield atoms which would not be further divisible. The word 'atom' has been derived from the Greek word 'a-tomio' which means 'uncut-able' or 'non-divisible'. These earlier ideas were mere speculations and there was no way to test them experimentally. These ideas remained dormant for a very long time and were revived again by scientists in the nineteenth century.

The atomic theory of matter was first proposed on a firm scientific basis by John Dalton, a British school teacher in 1808. His theory, called **Dalton's atomic theory**, regarded the atom as the ultimate particle of matter (Unit 1). Dalton's atomic theory was able to explain the law of conservation of mass, law of constant composition and law of multiple proportion very successfully. However, it failed to explain the results of many experiments, for example, it was known that substances like glass or ebonite when rubbed with silk or fur get electrically charged.

In this unit we start with the experimental observations made by scientists towards the end of nineteenth and beginning of twentieth century. These established that atoms are made of sub-atomic particles, i.e., electrons, protons and neutrons — a concept very different from that of Dalton.

2.1 Discovery of Sub-atomic Particles

An insight into the structure of atom was obtained from the experiments on electrical discharge through gases. Before we discuss these results we need to keep in mind a basic rule regarding the behaviour of charged particles : "Like charges repel each other and unlike charges attract each other".

2.1.1 Discovery of Electron

In 1830, Michael Faraday showed that if electricity is passed through a

solution of an electrolyte, chemical reactions occurred at the electrodes, which resulted in the liberation and deposition of matter at the electrodes. He formulated certain laws which you will study in class XII. These results suggested the particulate nature of electricity.

In mid 1850s many scientists mainly Faraday began to study electrical discharge in partially evacuated tubes, known as **cathode ray discharge tubes**. It is depicted in Fig. 2.1. A cathode ray tube is made of glass containing two thin pieces of metal, called electrodes, sealed in it. The electrical discharge through the gases could be observed only at very low pressures and at very high voltages. The pressure of different gases could be adjusted by evacuation of the glass tubes. When sufficiently high voltage is applied across the electrodes, current starts flowing through a stream of particles moving in the tube from the negative electrode (cathode) to the positive electrode (anode). These were called **cathode rays or cathode ray particles**. The flow of current from cathode to anode was further checked by making a hole in the anode and coating the tube behind anode with phosphorescent material zinc sulphide. When these rays, after passing through anode, strike the zinc sulphide coating, a bright spot is developed on the coating [Fig. 2.1(b)].

The results of these experiments are summarised below.

(i) The cathode rays start from cathode and move towards the anode.

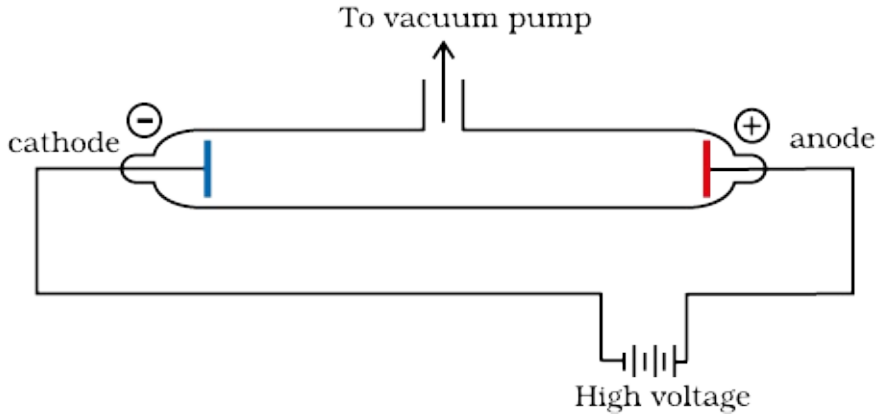


Fig. 2.1(b) A cathode ray discharge tube with perforated anode

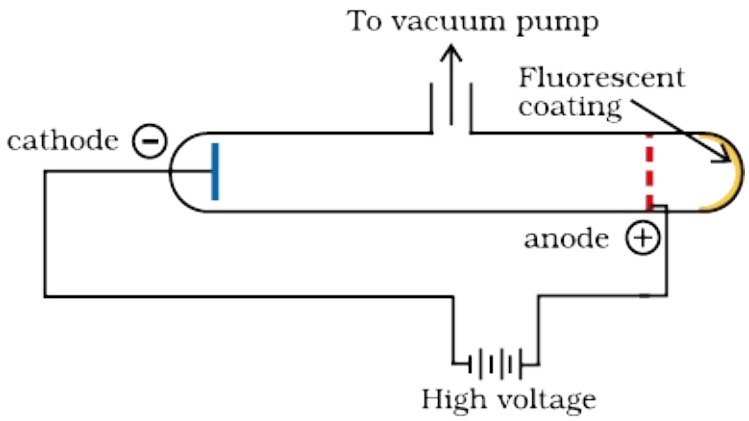


Fig. 2.1(a) A cathode ray discharge tube

(ii) These rays themselves are not visible but their behaviour can be observed with the help of certain kind of materials (fluorescent or phosphorescent) which glow when hit by them. Television picture tubes are cathode ray tubes and television pictures result due to fluorescence on the television screen coated with certain fluorescent or phosphorescent materials.

(iii) In the absence of electrical or magnetic field, these rays travel in straight lines (Fig. 2.2).

(iv) In the presence of electrical or magnetic field, the behaviour of cathode rays are similar to that expected from negatively charged particles, suggesting that the cathode rays consist of negatively charged particles, called **electrons.**

(v) The characteristics of cathode rays (electrons) do not depend upon the material of electrodes and the nature of the gas present in the cathode ray tube.

Thus, we can conclude that electrons are basic constituent of all the atoms.

2.1.2 Charge to Mass Ratio of Electron

In 1897, British physicist J.J. Thomson measured the ratio of electrical charge (e) to the mass of electron (m_e) by using cathode ray tube and applying electrical and magnetic field perpendicular to each other as well as to the path of electrons (Fig. 2.2). When only electric field is applied, the electrons deviate from their path and hit the cathode ray tube at point A (Fig. 2.2). Similarly when only magnetic field is applied, electron strikes the cathode ray tube at point C. By carefully balancing the electrical and magnetic field strength, it is possible to bring back the electron to the path which is followed in the absence of electric or magnetic field and they hit the screen at point B. Thomson argued that the amount of deviation of the particles from their path in the presence of electrical or magnetic field depends upon:

(i) the magnitude of the negative charge on the particle, greater the magnitude of the charge on the particle, greater is the interaction with the electric or magnetic field and thus greater is the deflection.

(ii) the mass of the particle — lighter the particle, greater the deflection.

(iii) the strength of the electrical or magnetic field — the deflection of electrons from its original path increases with the increase in the voltage across the electrodes, or the strength of the magnetic field.

By carrying out accurate measurements on the amount of deflections observed by the electrons on the electric field strength or magnetic field strength, Thomson was able to determine the value of e/m_e as:

$$\frac{e}{m_e} = 1.758820 \times 10^{11} \text{ C kg}^{-1} \qquad (2.1)$$

Where m_e is the mass of the electron in kg and e is the magnitude of the charge on the electron in coulomb (C). Since electrons are negatively charged, the charge on electron is –e.

2.1.3 Charge on the Electron

R.A. Millikan (1868-1953) devised a method known as oil drop experiment (1906-14), to determine the charge on the electrons. He found the charge on the electron to be

-1.6×10^{-19} C. The present accepted value of electrical charge is $-1.602176 \times 10^{-19}$ C. The mass of the electron (m_e) was determined by combining these results with Thomson's value of e/m_e ratio.

$$m_e = \frac{e}{e/m_e} = \frac{1.602176 \times 10^{-19}\text{C}}{1.758820 \times 10^{11}\text{C kg}^{-1}}$$

$$= 9.1094 \times 10^{-31}\text{ kg} \qquad (2.2)$$

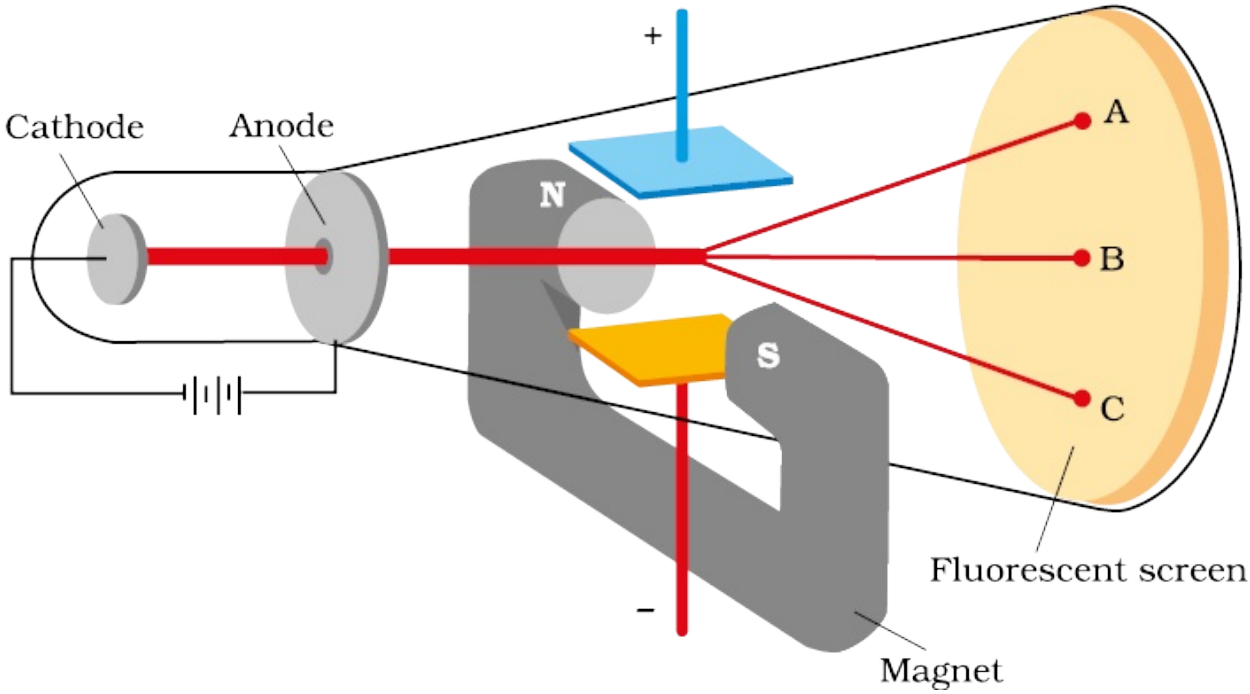


Fig. 2.2 The apparatus to determine the charge to the mass ratio of electron

2.1.4 Discovery of Protons and Neutrons

Electrical discharge carried out in the modified cathode ray tube led to the discovery of **canal rays** carrying positively charged particles. The characteristics of these positively charged particles are listed below.

(i) Unlike cathode rays, mass of positively charged particles depends

upon the nature of gas present in the cathode ray tube. These are simply the positively charged gaseous ions.

(ii) The charge to mass ratio of the particles depends on the gas from which these originate.

(iii) Some of the positively charged particles carry a multiple of the fundamental unit of electrical charge.

(iv) The behaviour of these particles in the magnetic or electrical field is opposite to that observed for electron or cathode rays.

The smallest and lightest positive ion was obtained from hydrogen and was called **proton**. This positively charged particle was characterised in 1919. Later, a need was felt for the presence of electrically neutral particle as one of the constituent of atom. These particles were discovered by Chadwick (1932) by bombarding a thin sheet of beryllium by α-particles. When electrically neutral particles having a mass slightly greater than that of protons were emitted. He named these particles as **neutrons**. The important properties of all these fundamental particles are given in Table 2.1.

2.2 Atomic Models

Observations obtained from the experiments mentioned in the previous sections have suggested that Dalton's indivisible atom is composed of sub-atomic particles carrying positive and negative charges. The major problems before the scientists after the discovery of sub-atomic particles were:

• to account for the stability of atom,

• to compare the behaviour of elements in terms of both physical and chemical properties,

• to explain the formation of different kinds of molecules by the combination of different atoms and,

• to understand the origin and nature of the characteristics of

electromagnetic radiation absorbed or emitted by atoms.

Millikan's Oil Drop Method

In this method, oil droplets in the form of mist, produced by the atomiser, were allowed to enter through a tiny hole in the upper plate of electrical condenser. The downward motion of these droplets was viewed through the telescope, equipped with a micrometer eye piece. By measuring the rate of fall of these droplets, Millikan was able to measure the mass of oil droplets. The air inside the chamber was ionized by passing a beam of X-rays through it. The electrical charge on these oil droplets was acquired by collisions with gaseous ions. The fall of these charged oil droplets can be retarded, accelerated or made stationary depending upon the charge on the droplets and the polarity and strength of the voltage applied to the plate. By carefully measuring the effects of electrical field strength on the motion of oil droplets, Millikan concluded that the magnitude of electrical charge, q, on the droplets is always an integral multiple of the electrical charge, e, that is, q = n e, where n = 1, 2, 3... .

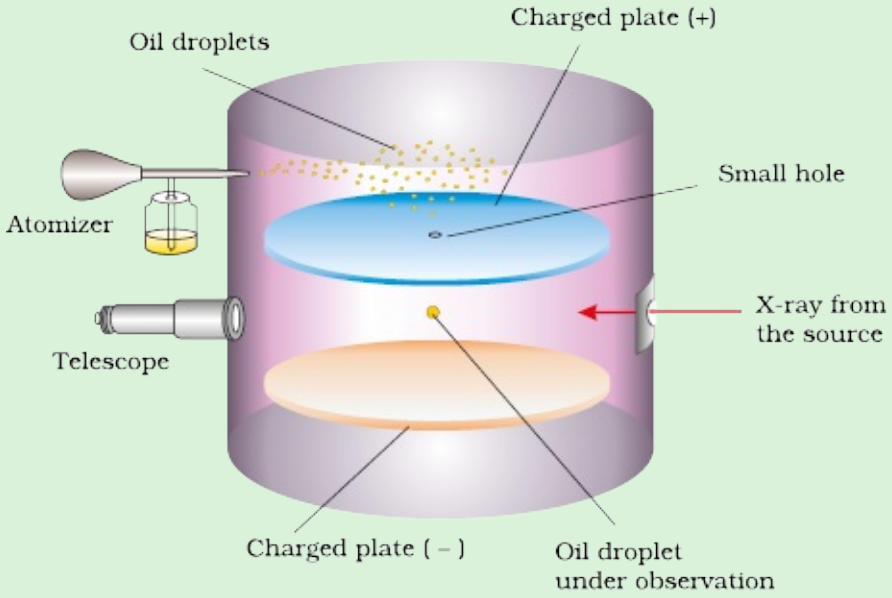


Fig. 2.3 The Millikan oil drop apparatus for measuring charge 'e'. In chamber, the forces acting on oil drop are: gravitational, electrostatic due to electrical field and a viscous drag force when the oil drop is moving.

Table 2.1 Properties of Fundamental Particles

Name	Symbol	Absolute charge/C	Relative charge	Mass/kg	Mass/u	Approx. mass/u
Electron	e	-1.602176×10^{-19}	−1	9.109382×10^{-31}	0.00054	0
Proton	p	$+1.602176\times10^{-19}$	+1	1.6726216×10^{-27}	1.00727	1
Neutron	n	0	0	1.674927×10^{-27}	1.00867	1

Different atomic models were proposed to explain the distributions of these charged particles in an atom. Although some of these models were not able to explain the stability of atoms, two of these models, one proposed by J.J. Thomson and the other proposed by Ernest Rutherford are discussed below.

2.2.1 Thomson Model of Atom

J. J. Thomson, in 1898, proposed that an atom possesses a spherical shape (radius approximately 10^{-10} m) in which the positive charge is uniformly distributed. The electrons are embedded into it in such a manner as to give the most stable electrostatic arrangement (Fig. 2.4). Many different names are given to this model, for example, **plum pudding, raisin pudding or watermelon.** This model can be visualised as a pudding or watermelon of positive charge with plums or seeds (electrons) embedded into it. An important feature of this model is that the mass of the atom is assumed to be uniformly distributed over the atom. Although this model was able to explain the overall neutrality of the atom, but was not consistent with the results of later experiments. Thomson was awarded Nobel Prize for physics in 1906, for his theoretical and experimental investigations on the conduction of electricity by gases.

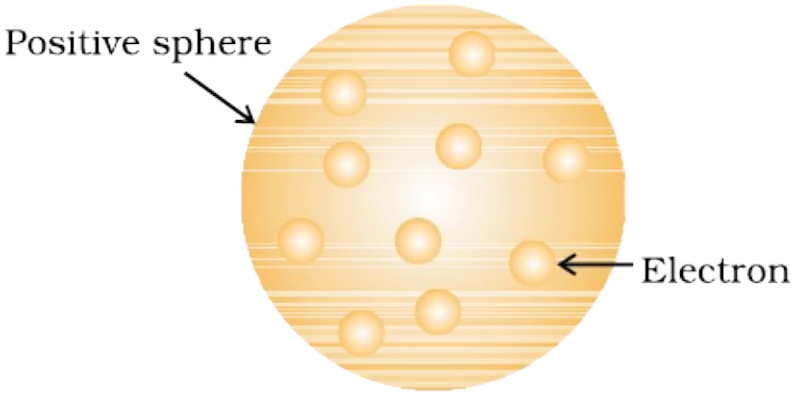


Fig.2.4 Thomson model of atom

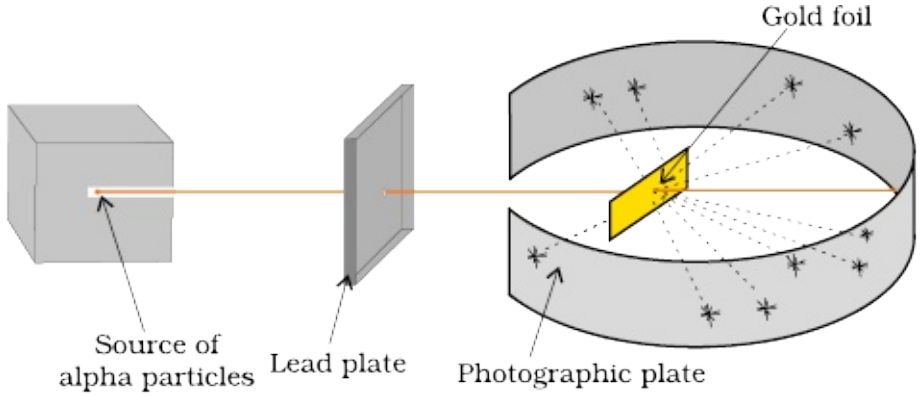
In the later half of the nineteenth century different kinds of rays were discovered, besides those mentioned earlier. Wilhalm Röentgen (1845-1923) in 1895 showed that when electrons strike a material in the cathode ray tubes, produce rays which can cause fluorescence in the fluorescent materials placed outside the cathode ray tubes. Since Röentgen did not know the nature of the radiation, he named them X-rays and the name is still carried on. It was noticed that X-rays are produced effectively when electrons strike the dense metal anode, called targets. These are not deflected by the electric and magnetic fields and have a very high penetrating power through the matter and that is the reason that these rays are used to study the interior of the objects. These rays are of very short wavelengths (~0.1 nm) and possess electro-magnetic character (Section 2.3.1).

Henri Becqueral (1852-1908) observed that there are certain elements which emit radiation on their own and named this phenomenon as **radioactivity** and the elements known as **radioactive elements.** This field was developed by Marie Curie, Piere Curie, Rutherford and Fredrick Soddy. It was observed that three kinds of rays i.e., α, β- and γ-rays are emitted. Rutherford found that α-rays consists of high energy particles carrying two units of positive charge and four unit of atomic mass. He concluded that α- particles are helium nuclei as when α- particles combined with two electrons yielded helium gas. β-rays are negatively charged particles similar to electrons. The γ-rays are high energy radiations like X-rays, are neutral in nature and do not consist of particles. As regards penetrating power, α-particles are the least, followed by β-rays (100 times that of α–particles) and γ-rays (1000 times of

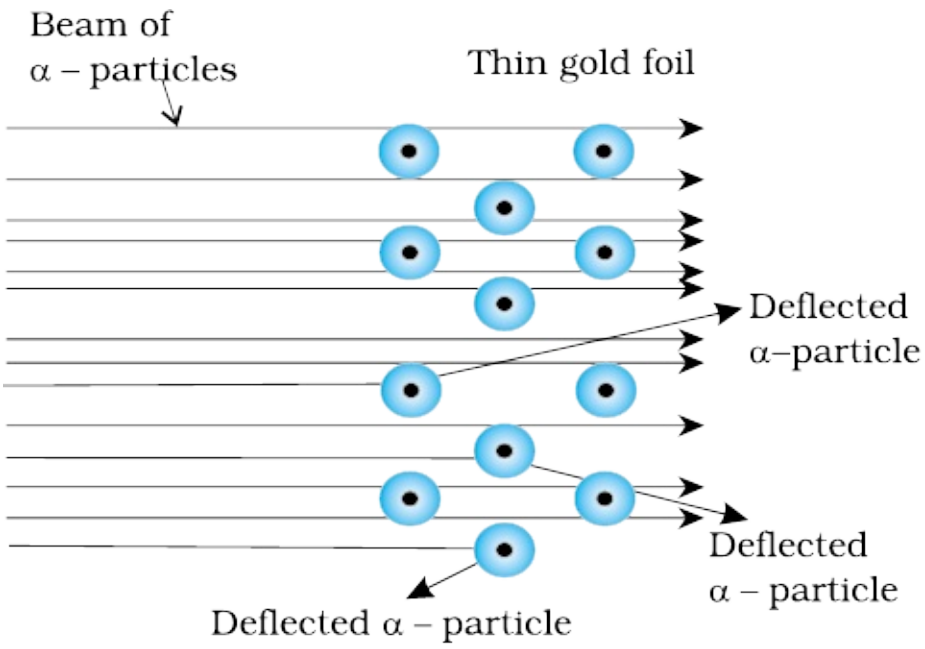
that α-particles).

2.2.2 Rutherford's Nuclear Model of Atom

Rutherford and his students (Hans Geiger and Ernest Marsden) bombarded very thin gold foil with α–particles. Rutherford's famous **α–particle scattering experiment** is represented in Fig. 2.5. A stream of high energy α–particles from a radioactive source was directed at a thin foil (thickness ~ 100 nm) of gold metal. The thin gold foil had a circular fluorescent zinc sulphide screen around it. Whenever α–particles struck the screen, a tiny flash of light was produced at that point.



B. Schematic molecular view of the gold foil



A. Rutherford's scattering experiment

Fig. 2.5 Schematic view of Rutherford's scattering experiment. When a beam of alpha (α) particles is "shot" at a thin gold foil, most of them pass through without much effect. Some, however, are deflected.

The results of scattering experiment were quite unexpected. According to Thomson model of atom, the mass of each gold atom in the foil should have been spread evenly over the entire atom, and α– particles had enough energy to pass directly through such a uniform distribution of mass. It was expected that the particles would slow down and change directions only by a small angles as they passed through the foil. It was observed that:

(i) most of the α–particles passed through the gold foil undeflected.

(ii) a small fraction of the α–particles was deflected by small angles.

(iii) a very few α–particles (~1 in 20,000) bounced back, that is, were deflected by nearly 180°.

On the basis of the observations, Rutherford drew the following conclusions regarding the structure of atom:

(i) Most of the space in the atom is empty as most of the α–particles passed through the foil undeflected.

(ii) A few positively charged α–particles were deflected. The deflection must be due to enormous repulsive force showing that the positive charge of the atom is not spread throughout the atom as Thomson had presumed. The positive charge has to be concentrated in a very small volume that repelled and deflected the positively charged α–particles.

(iii) Calculations by Rutherford showed that the volume occupied by the nucleus is negligibly small as compared to the total volume of the atom. The radius of the atom is about 10^{-10} m, while that of nucleus is 10^{-15} m. One can appreciate this difference in size by realising that if a

cricket ball represents a nucleus, then the radius of atom would be about 5 km.

On the basis of above observations and conclusions, Rutherford proposed the nuclear model of atom. According to this model:

(i) The positive charge and most of the mass of the atom was densely concentrated in extremely small region. This very small portion of the atom was called **nucleus** by Rutherford.

(ii) The nucleus is surrounded by electrons that move around the nucleus with a very high speed in circular paths called **orbits**. Thus, Rutherford's model of atom resembles the solar system in which the nucleus plays the role of sun and the electrons that of revolving planets.

(iii) Electrons and the nucleus are held together by electrostatic forces of attraction.

2.2.3 Atomic Number and Mass Number

The presence of positive charge on the nucleus is due to the protons in the nucleus. As established earlier, the charge on the proton is equal but opposite to that of electron. The number of protons present in the nucleus is equal to atomic number (Z). For example, the number of protons in the hydrogen nucleus is 1, in sodium atom it is 11, therefore their atomic numbers are 1 and 11 respectively. In order to keep the electrical neutrality, the number of electrons in an atom is equal to the number of protons (atomic number, Z). For example, number of electrons in hydrogen atom and sodium atom are 1 and 11 respectively.

Atomic number (Z**) = number of protons in the nucleus of an atom = number of electrons in a nuetral atom** (2.3)

While the positive charge of the nucleus is due to protons, the mass of the nucleus, due to protons and neutrons. As discussed earlier protons and neutrons present in the nucleus are collectively known as **nucleons**. The total number of nucleons is termed as **mass number (A)** of the

atom.

mass number (A) = number of protons (*Z*)
+ number of neutrons (n) (2.4)

2.2.4 Isobars and Isotopes

The composition of any atom can be represented by using the normal element symbol (X) with super-script on the left hand side as the atomic mass number (A) and subscript (Z) on the left hand side as the atomic number (i.e., ${}^{A}_{Z}X$).

Isobars are the atoms with same mass number but different atomic number for example, ${}_{6}{}^{14}C$ and ${}_{7}{}^{14}N$. On the other hand, atoms with identical atomic number but different atomic mass number are known as **Isotopes**. In other words (according to equation 2.4), it is evident that difference between the isotopes is due to the presence of different number of neutrons present in the nucleus. For example, considering of hydrogen atom again, 99.985% of hydrogen atoms contain only one proton. This isotope is called **protium (${}_{1}{}^{1}H$)**. Rest of the percentage of hydrogen atom contains two other isotopes, the one containing 1 proton and 1 neutron is called **deuterium** (${}_{1}{}^{2}D$, 0.015%) and the other one possessing 1 proton and 2 neutrons is called **tritium (${}_{1}{}^{3}T$)**. The latter isotope is found in trace amounts on the earth. Other examples of commonly occuring isotopes are: carbon atoms containing 6, 7 and 8 neutrons besides 6 protons (${}^{12}_{6}C$, ${}^{13}_{6}C$, ${}^{14}_{6}C$); chlorine atoms containing 18 and 20 neutrons besides 17 protons (${}^{35}_{17}Cl$, ${}^{37}_{17}Cl$).

Lastly an important point to mention regarding isotopes is that chemical properties of atoms are controlled by the number of electrons, which are determined by the number of protons in the nucleus. Number of neutrons present in the nucleus have very little effect on the chemical properties of

an element. Therefore, all the isotopes of a given element show same chemical behaviour.

Problem 2.1

Calculate the number of protons, neutrons and electrons in $^{80}_{35}\mathrm{Br}$.

Solution

In this case, $^{80}_{35}\mathrm{Br}$, Z = 35, A = 80, species is neutral

Number of protons = number of electrons = Z = 35

Number of neutrons = 80 – 35 = 45, (equation 2.4)

Problem 2.2

The number of electrons, protons and neutrons in a species are equal to 18, 16 and 16 respectively. Assign the proper symbol to the species.

Solution

The atomic number is equal to

number of protons = 16. The element is sulphur (S).

Atomic mass number = number of protons + number of neutrons

= 16 + 16 = 32

Species is not neutral as the number of protons is not equal to electrons. It is anion (negatively charged) with charge equal to excess electrons = 18 – 16 = 2. Symbol is $^{32}_{16}\mathrm{S}^{2-}$

.

Note : Before using the notation $^{A}_{Z}\mathrm{X}$, find out whether the species is a neutral atom, a cation or an anion. If it is a neutral atom, equation (2.3) is valid, i.e., number of protons = number of electrons = atomic number. If the species is an ion, determine whether the number of protons are larger (cation, positive ion) or smaller (anion, negative ion) than the number of electrons. Number of neutrons is always given by A–Z, whether the species is neutral or ion.

2.2.5 Drawbacks of Rutherford Model

As you have learnt above, Rutherford nuclear model of an atom is like a small scale solar system with the nucleus playing the role of the massive sun and the electrons being similar to the lighter planets. When classical mechanics* is applied to the solar system, it shows that the planets describe well-defined orbits around the sun. The gravitational force between the planets is given by the expression $\left(G.\frac{m_1 m_2}{r^2}\right)$ where m_1 and m_2 are the masses, r is the distance of separation of the masses and G is the gravitational constant. The theory can also calculate precisely the planetary orbits and these are in agreement with the experimental measurements.

The similarity between the solar system and nuclear model suggests that electrons should move around the nucleus in well defined orbits. Further, the coulomb force (kq_1q_2/r^2 where q_1 and q_2 are the charges, r is the distance of separation of the charges and k is the proportionality constant) between electron and the nucleus is mathematically similar to the gravitational force. However, when a body is moving in an orbit, it undergoes acceleration even if it is moving with a constant speed in an orbit because of changing direction. So an electron in the nuclear model describing planet like orbits is under acceleration. According to the electromagnetic theory of Maxwell, charged particles when accelerated should emit electromagnetic radiation (This feature does not exist for planets since they are uncharged). Therefore, an electron in an orbit will emit radiation, the energy carried by radiation comes from electronic motion. The orbit will thus continue to shrink. Calculations show that it should take an electron only 10^{-8} s to spiral into the nucleus. But this does not happen. Thus, the Rutherford model cannot explain the stability of an atom.

If the motion of an electron is described on the basis of the classical

mechanics and electromagnetic theory, you may ask that since the motion of electrons in orbits is leading to the instability of the atom, then why not consider electrons as stationary around the nucleus. If the electrons were stationary, electrostatic attraction between
the dense nucleus and the electrons would pull the electrons toward the nucleus to forma miniature version of Thomson's model of atom.

* *Classical mechanics is a theoretical science based on Newton's laws of motion. It specifies the laws of motion of macroscopic objects.*

Another serious drawback of the Rutherford model is that it says nothing about distribution of the electrons around the nucleus and the energies of these electrons.

2.3 Developments Leading to the Bohr's Model of Atom

Historically, results observed from the studies of interactions of radiations with matter have provided immense information regarding the structure of atoms and molecules. Neils Bohr utilised these results to improve upon the model proposed by Rutherford. Two developments played a major role in the formulation of Bohr's model of atom. These were:

(i) Dual character of the electromagnetic radiation which means that radiations possess both wave like and particle like properties, and

(ii) Experimental results regarding atomic spectra.

First, we will discuss about the duel nature of electromagnetic radiations. Experimental results regarding atomic spectra will be discussed in Section 2.4.

2.3.1 Wave Nature of Electromagnetic Radiation

In the mid-nineteenth century, physicists actively studied absorption and emission of radiation by heated objects. These are called thermal radiations. They tried to find out of what the thermal radiation is made. It

is now a well-known fact that thermal radiations consist of electromagnetic waves of various frequencies or wavelengths. It is based on a number of modern concepts, which were unknown in the mid-nineteenth century. First active study of thermal radiation laws occured in the 1850's and the theory of electromagnetic waves and the emission of such waves by accelerating charged particles was developed in the early 1870's by James Clerk Maxwell, which was experimentally confirmed later by Heinrich Hertz. Here, we will learn some facts about electromagnetic radiations.

James Maxwell (1870) was the first to give a comprehensive explanation about the interaction between the charged bodies and the behaviour of electrical and magnetic fields on macroscopic level. He suggested that when electrically charged particle moves under accelaration, alternating electrical and magnetic fields are produced and transmitted. These fields are transmitted in the forms of waves called **electromagnetic waves** or **electromagnetic radiation**.

Light is the form of radiation known from early days and speculation about its nature dates back to remote ancient times. In earlier days (Newton) light was supposed to be made of particles (corpuscules). It was only in the 19th century when wave nature of light was established.

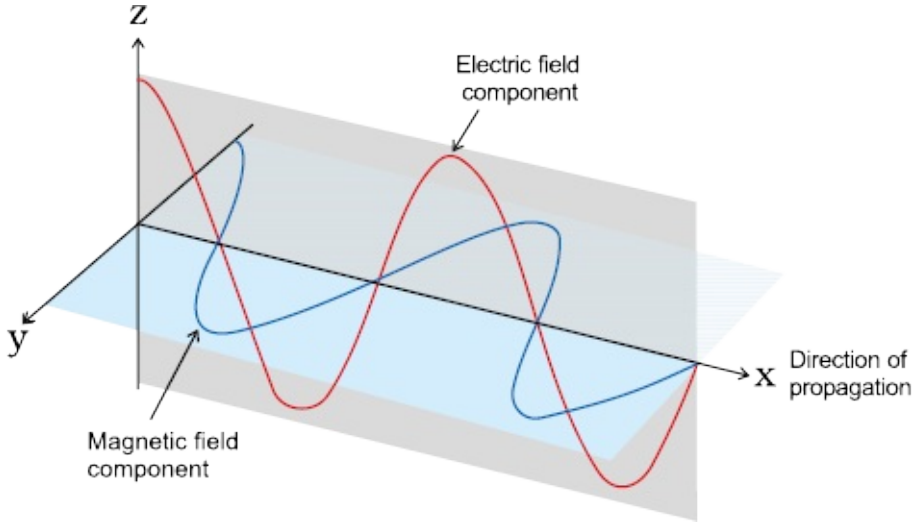


Fig.2.6 The electric and magnetic field components of an electromagnetic wave. These

components have the same wavelength, frequency, speed and amplitude, but they vibrate in two mutually perpendicular planes.

Maxwell was again the first to reveal that light waves are associated with oscillating electric and magnetic character (Fig. 2.6). Although electromagnetic wave motion is complex in nature, we will consider here only a few simple properties.

(i) The oscillating electric and magnetic fields produced by oscillating charged particles are perpendicular to each other and both are perpendicular to the direction of propagation of the wave. Simplified picture of electromagnetic wave is shown in Fig. 2.6.

(ii) Unlike sound waves or waves produced in water, electromagnetic waves do not require medium and can move in vacuum.

(iii) It is now well established that there are many types of electromagnetic radiations, which differ from one another in wavelength (or frequency). These constitute what is called **electromagnetic spectrum** (Fig. 2.7). Different regions of the spectrum are identified by different names. Some examples are: radio frequency region around 10^6 Hz, used for broadcasting; microwave region around 10^{10} Hz used for radar; infrared region around 10^{13} Hz used for heating; ultraviolet region around 10^{16}Hz a component of sun's radiation. The small portion around 10^{15} Hz, is what is ordinarily called **visible light**. It is only this part which our eyes can see (or detect). Special instruments are required to detect non-visible radiation.

(iv) Different kinds of units are used to represent electromagnetic radiation.

These radiations are characterised by the properties, namely, frequency (v) and wavelength (λ).

The SI unit for frequency (v) is hertz (Hz, s^{-1}), after Heinrich Hertz. It is

defined as the number of waves that pass a given point in one second. Wavelength should have the units of length and as you know that the SI units of length is meter (m). Since electromagnetic radiation consists of different kinds of waves of much smaller wavelengths, smaller units are used. Fig.2.7 shows various types of electro-magnetic radiations which differ from one another in wavelengths and frequencies.

In vaccum all types of electromagnetic radiations, regardless of wavelength, travel at the same speed, i.e., 3.0×10^8 m s^{-1} (2.997925×10^8 m s^{-1}, to be precise). This is called **speed of light** and is given the symbol 'c'. The frequency (ν), wavelength (λ) and velocity of light (c) are related by the equation (2.5).

$$c = \nu \lambda \qquad (2.5)$$

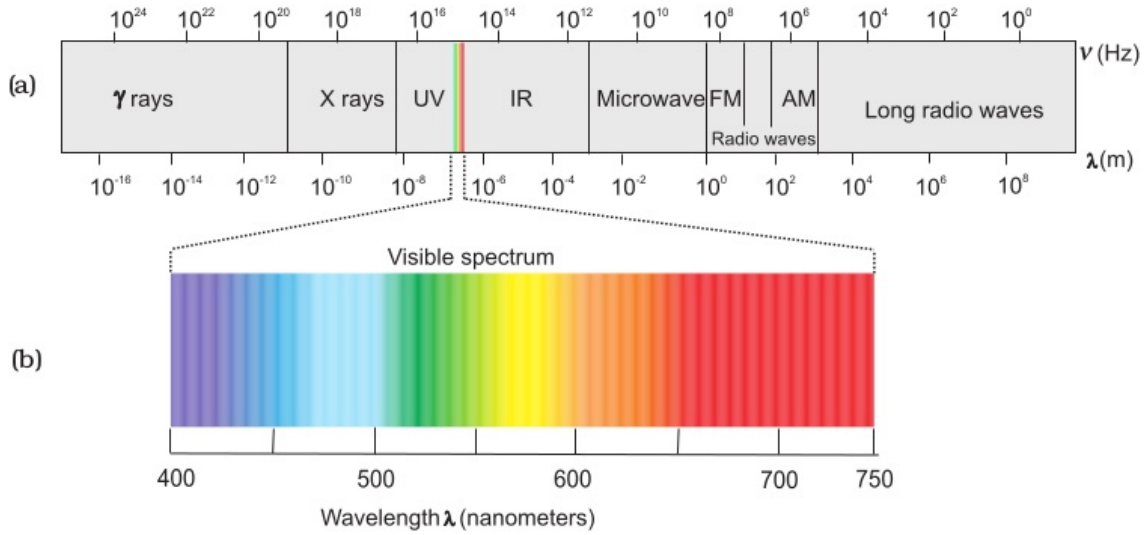


Fig. 2.7 (a) The spectrum of electromagnetic radiation. (b) Visible spectrum. The visible region is only a small part of the entire spectrum.

The other commonly used quantity specially in spectroscopy, is the **wavenumber** ($\bar{\nu}$). It is defined as the number of wavelengths per unit length. Its units are reciprocal of wavelength unit, i.e., m^{-1}. However commonly used unit is cm^{-1} (not SI unit).

Problem 2.3

The Vividh Bharati station of All India Radio, Delhi, broadcasts on a frequency of 1,368 kHz (kilo hertz). Calculate the wavelength of the electromagnetic radiation emitted by transmitter. Which part of the electromagnetic spectrum does it belong to?

Solution

The wavelength, λ, is equal to c/v, where c is the speed of electromagnetic radiation in vacuum and v is the frequency. Substituting the given values, we have

$$\lambda = \frac{c}{\upsilon}$$

$$= \frac{3.00 \times 10^{8}\,\mathrm{m\,s^{-1}}}{1368\ \mathrm{kHz}}$$

$$= \frac{3.00 \times 10^{8}\,\mathrm{m\,s^{-1}}}{1368 \times 10^{3}\,\mathrm{s^{-1}}}$$

$$= 219.3\,\mathrm{m}$$

This is a characteristic radiowave wavelength.

Problem 2.4

The wavelength range of the visible spectrum extends from violet (400 nm) to red (750 nm). Express these wavelengths in frequencies (Hz). (1nm = 10^{-9} m)

Solution

Using equation 2.5, frequency of violet light

$$\nu = \frac{c}{\lambda} = \frac{3.00 \times 10^{8}\,\mathrm{m\,s^{-1}}}{400 \times 10^{-9}\,\mathrm{m}}$$

$$= 7.50 \times 10^{14}\,\mathrm{Hz}$$

= 7.50 × 10^{14} Hz

Frequency of red light

$$\nu = \frac{c}{\lambda} = \frac{3.00 \times 10^{8}\,\mathrm{m\,s^{-1}}}{750 \times 10^{-9}\,\mathrm{m}} = 4.00 \times 10^{14}\,\mathrm{Hz}$$

The range of visible spectrum is from

4.0 × 10^{14} to 7.5 × 10^{14} Hz in terms of frequency units.

Problem 2.5

Calculate (a) wavenumber and (b) frequency of yellow radiation having wavelength 5800 Å.

Solution

(a) Calculation of wavenumber ($\bar{\nu}$)

$\lambda = 5800 Å = 5800 \times 10^{-8}$ cm

$= 5800 \times 10^{-10}$ m

$$\bar{\nu} = \frac{1}{\lambda} = \frac{1}{5800 \times 10^{-10}\ \text{m}}$$

$$= 1.724 \times 10^{6}\ \text{m}^{-1}$$

$$= 1.724 \times 10^{4}\ \text{cm}^{-1}$$

(b) Calculation of the frequency (ν)

$$\bar{\nu} = \frac{c}{\lambda} = \frac{3 \times 10^{8}\ \text{m s}^{-1}}{5800 \times 10^{-10}\ \text{m}} = 5.172 \times 10^{14}\ \text{s}^{-1}$$

2.3.2 Particle Nature of Electromagnetic Radiation: Planck's Quantum Theory

Some of the experimental phenomenon such as diffraction* and interference** can be explained by the wave nature of the electromagnetic radiation. However, following are some of the observations which could not be explained with the help of even the electromagentic theory of 19th century physics (known as classical physics):

(i) the nature of emission of radiation from hot bodies (black -body radiation)

(ii) ejection of electrons from metal surface when radiation strikes it (photoelectric effect)

(iii) variation of heat capacity of solids as a function of temperature

(iv) Line spectra of atoms with special reference to hydrogen.

* Diffraction is the bending of wave around an obstacle.

** Interference is the combination of two waves of the same or different frequencies to give a wave whose distribution at each point in space is the algebraic or vector sum of disturbances at that point resulting from

each interfering wave.

These phenomena indicate that the system can take energy only in discrete amounts. All possible energies cannot be taken up or radiated.

It is noteworthy that the first concrete explanation for the phenomenon of the black body radiation mentioned above was given by Max Planck in 1900. Let us first try to understand this phenomenon, which is given below:

Hot objects emit electromagnetic radiations over a wide range of wavelengths. At high temperatures, an appreciable proportion of radiation is in the visible region of the spectrum. As the temperature is raised, a higher proportion of short wavelength (blue light) is generated. For example, when an iron rod is heated in a furnace, it first turns to dull red and then progressively becomes more and more red as the temperature increases. As this is heated further, the radiation emitted becomes white and then becomes blue as the temperature becomes very high. This means that red radiation is most intense at a particular temperature and the blue radiation is more intense at another temperature. This means intensities of radiations of different wavelengths emitted by hot body depend upon its temperature. By late 1850's it was known that objects made of different material and kept at different temperatures emit different amount of radiation. Also, when the surface of an object is irradiated with light (electromagnetic radiation), a part of radiant energy is generally reflected as such, a part is absorbed and a part of it is transmitted. The reason for incomplete absorption is that ordinary objects are as a rule imperfect absorbers of radiation. An ideal body, which emits and absorbs radiations of all frequencies uniformly, is called a black body and the radiation emitted by such a body is called black body radiation. In practice, no such body exists. Carbon black approximates fairly closely to black body. A good physical approximation to a black body is a cavity with a tiny hole, which has no other opening. Any ray entering the hole

will be reflected by the cavity walls and will be eventually absorbed by the walls. A black body is also a perfect radiator of radiant energy. Furthermore, a black body is in thermal equilibrium with its surroundings. It radiates same amount of energy per unit area as it absorbs from its surrounding in any given time. The amount of light emitted (intensity of radiation) from a black body and its spectral distribution depends only on its temperature. At a given temperature, intensity of radiation emitted increases with the increase of wavelength, reaches a maximum value at a given wavelength and then starts decreasing with further increase of wavelength, as shown in Fig. 2.8. Also, as the temperature increases, maxima of the curve shifts to short wavelength. Several attempts were made to predict the intensity of radiation as a function of wavelength.

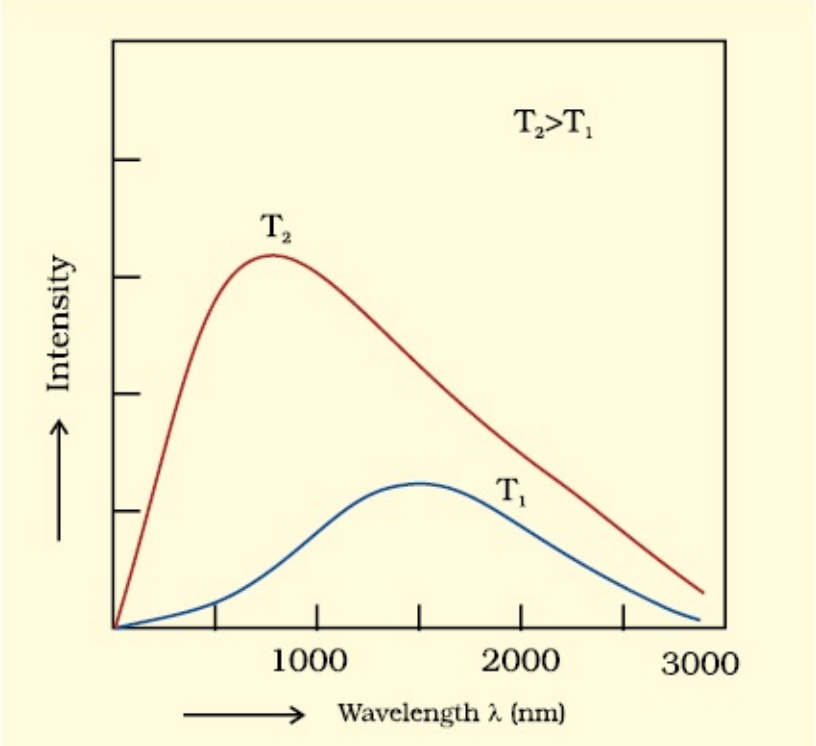


Fig. 2.8 Wavelength-intensity relationship

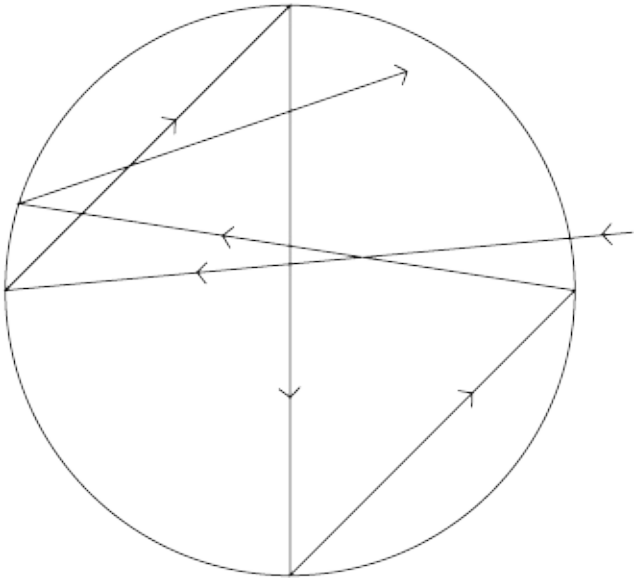


Fig. 2.8(a) Black body

But the results of the above experiment could not be explained satisfactorily on the basis of the wave theory of light. Max Planck arrived at a satisfactory relationship by making an assumption that absorption and emmission of radiation arises from oscillator i.e., atoms in the wall of black body. Their frequency of oscillation is changed by interaction with oscilators of electromagnetic radiation. Planck assumed that radiation could be sub-divided into discrete chunks of energy. He suggested that atoms and molecules could emit or absorb energy only in discrete quantities and not in a continuous manner. He gave the name **quantum** to the smallest quantity of energy that can be emitted or absorbed in the form of electromagnetic radiation. The energy (E) of a quantum of radiation is proportional to its frequency (v) and is expressed by equation (2.6).

$E = h\upsilon$ (2.6)

The proportionality constant, 'h' is known as Planck's constant and has the value 6.626×10^{-34} J s.

With this theory, Planck was able to explain the distribution of intensity in the radiation from black body as a function of frequency or wavelength at different temperatures.

Quantisation has been compared to standing on a staircase. A person can stand on any step of a staircase, but it is not possible for him/her to stand in between the two steps. The energy can take any one of the values from the following set, but cannot take on any values between them.

E = 0, hu, 2hu, 3hu....nhu.....

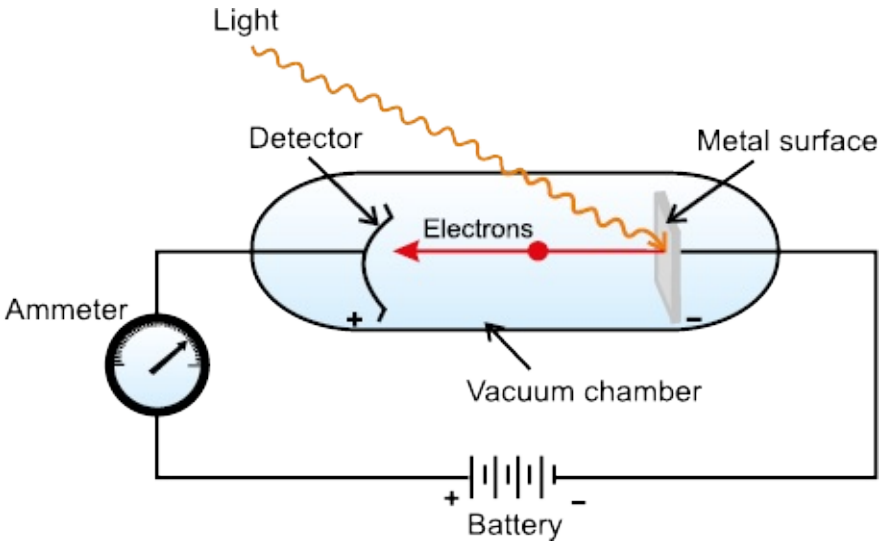


Fig.2.9 Equipment for studying the photoelectric effect. Light of a particular frequency strikes a clean metal surface inside a vacuum chamber. Electrons are ejected from the metal and are counted by a detector that measures their kinetic energy.



Max Planck

(1858 – 1947)

Max Planck, a German physicist, received his Ph.D in theoretical physics from the University of Munich in 1879. In 1888, he was appointed Director of the Institute of Theoretical Physics at the University of Berlin. Planck was awarded the Nobel Prize in Physics in 1918 for his quantum theory. Planck also made significant contributions in thermodynamics and other areas of physics.

Photoelectric Effect

In 1887, H. Hertz performed a very interesting experiment in which electrons (or electric current) were ejected when certain metals (for example potassium, rubidium, caesium etc.) were exposed to a beam of light as shown

in Fig.2.9. The phenomenon is called **Photoelectric effect**. The results observed in this experiment were:

(i) The electrons are ejected from the metal surface as soon as the beam of light strikes the surface, i.e., there is no time lag between the striking of light beam and the ejection of electrons from the metal surface.

(ii) The number of electrons ejected is proportional to the intensity or brightness of light.

(iii) For each metal, there is a characteristic minimum frequency, v_0 (also known as **threshold frequency**) below which photoelectric effect is not observed. At a frequency $v > v_0$, the ejected electrons come out with certain kinetic energy. The kinetic energies of these electrons increase with the increase of frequency of the light used.

All the above results could not be explained on the basis of laws of classical physics. According to latter, the energy content of the beam of light depends upon the brightness of the light. In other words, number of

electrons ejected and kinetic energy associated with them should depend on the brightness of light. It has been observed that though the number of electrons ejected does depend upon the brightness of light, the kinetic energy of the ejected electrons does not. For example, red light [v = (4.3 to 4.6) × 10^{14} Hz] of any brightness (intensity) may shine on a piece of potassium metal for hours but no photoelectrons are ejected. But, as soon as even a very weak yellow light (v = 5.1–5.2 × 10^{14} Hz) shines on the potassium metal, the photoelectric effect is observed. The threshold frequency (v_0) for potassium metal is 5.0×1014 Hz.

Table 2.2 Values of Work Function (W0) for a Few Metals

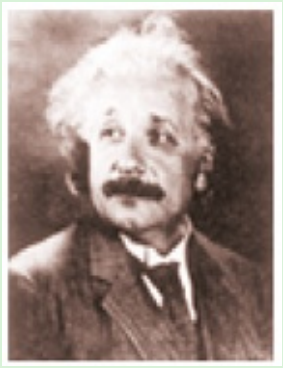
Metal	Li	Na	K	Mg	Cu	Ag
W_0 /eV	2.42	2.3	2.25	3.7	4.8	4.3

Einstein (1905) was able to explain the photoelectric effect using Planck's quantum theory of electromagnetic radiation as a starting point.
Shining a beam of light on to a metal surface can, therefore, be viewed as shooting a beam of particles, the photons. When a photon of sufficient energy strikes an electron in the atom of the metal, it transfers its energy instantaneously to the electron during the collision and the electron is ejected without any time lag or delay. Greater the energy possessed by the photon, greater will be transfer of energy to the electron and greater the kinetic energy of the ejected electron. In other words, kinetic energy of the ejected electron is proportional to the frequency of the electromagnetic radiation. Since the striking photon has energy equal to hv and the minimum energy required to eject the electron is hv_0 (also called work function, W0; Table 2.2), then the difference in energy
(hv – hv_0) is transferred as the kinetic energy of the photoelectron.

Following the conservation of energy principle, the kinetic energy of the ejected electron is given by the equation 2.7.

$$h\nu = h\nu_0 + \frac{1}{2}m_e v^2 \qquad (2.7)$$

where m_e is the mass of the electron and v is the velocity associated with the ejected electron. Lastly, a more intense beam of light consists of larger number of photons, consequently the number of electrons ejected is also larger as compared to that in an experiment in which a beam of weaker intensity of light is employed.



Albert Einstein

(1879-1955)

Albert Einstein, a German born American physicist, is regarded by many as one of the two great physicists the world has known (the other is Isaac Newton). His three research papers (on special relativity, Brownian motion and the photoelectric effect) which he published in 1905, while he was employed as a technical assistant in a Swiss patent office in Berne have profoundly influenced the development of physics. He received the Nobel Prize in Physics in 1921 for his explanation of the photoelectric effect.

Dual Behaviour of Electromagnetic Radiation

The particle nature of light posed a dilemma for scientists. On the one hand, it could explain the black body radiation and photoelectric effect

satisfactorily but on the other hand, it was not consistent with the known wave behaviour of light which could account for the phenomena of interference and diffraction. The only way to resolve the dilemma was to accept the idea that light possesses both particle and wave-like properties, i.e., light has dual behaviour. Depending on the experiment, we find that light behaves either as a wave or as a stream of particles. Whenever radiation interacts with matter, it displays particle like properties in contrast to the wavelike properties (interference and diffraction), which it exhibits when it propagates. This concept was totally alien to the way the scientists thought about matter and radiation and it took them a long time to become convinced of its validity. It turns out, as you shall see later, that some microscopic particles like electrons also exhibit this wave-particle duality.

Problem 2.6

Calculate energy of one mole of photons of radiation whose frequency is 5×10^{14} Hz.

Solution

Energy (E) of one photon is given by the expression

$E = hv$

$h = 6.626 \times 10^{-34}$ J s

$v = 5 \times 10^{14}$ s^{-1} (given)

$E = (6.626 \times 10^{-34}$ J s) $\times$ $(5 \times 10^{14}$ $s^{-1})$

$= 3.313 \times 10^{-19}$ J

Energy of one mole of photons

$= (3.313 \times 10^{-19}$ J) $\times$ $(6.022 \times 10^{23}$ $mol^{-1})$

$= 199.51$ kJ mol^{-1}

Problem 2.7

A 100 watt bulb emits monochromatic light of wavelength 400 nm. Calculate the number of

photons emitted per second by the bulb.

Solution

Power of the bulb = 100 watt

= 100 J s^{-1}

Energy of one photon E = hv = hc/λ

$$= \frac{6.626 \times 10^{-34}\ \text{J s} \times 3 \times 10^{8}\ \text{m s}^{-1}}{400 \times 10^{-9}\ \text{m}}$$

$$= 4.969 \times 10^{-19}\ \text{J}$$

Number of photons emitted

$$\frac{100\ \text{J s}^{-1}}{4.969 \times 10^{-19}\ \text{J}} = 2.012 \times 10^{20}\ \text{s}^{-1}$$

Problem 2.8

When electromagnetic radiation of wavelength 300 nm falls on the surface of sodium, electrons are emitted with a kinetic energy of 1.68 ×10^5 J mol^{-1}. What is the minimum energy needed to remove an electron from sodium? What is the maximum wavelength that will cause a photoelectron to be emitted?

Solution

The energy (E) of a 300 nm photon is given by

$$h\nu = hc/\lambda$$

$$= \frac{6.626 \times 10^{-34}\ \text{J s} \times 3.0 \times 10^{8}\ \text{m s}^{-1}}{300 \times 10^{-9}\ \text{m}}$$

= 6.626 × 10^{-19} J

The energy of one mole of photons

= 6.626 ×10^{-19} J × 6.022 ×10^{23} mol^{-1}

= 3.99 × 10^5 J mol^{-1}

The minimum energy needed to remove one mole of electrons from sodium

= (3.99 –1.68) 10^5 J mol^{-1}

= 2.31 × 10^5 J mol^{-1}

The minimum energy for one electron

$$= \frac{2.31 \times 10^5 \text{ J mol}^{-1}}{6.022 \times 10^{23} \text{ electrons mol}^{-1}}$$

$$= 3.84 \times 10^{-19} \text{ J}$$

This corresponds to the wavelength

$$\therefore \lambda = \frac{hc}{E}$$

$$= \frac{6.626 \times 10^{-34} \text{ J s} \times 3.0 \times 10^8 \text{ m s}^{-1}}{3.84 \times 10^{-19} \text{ J}}$$

= 517 nm

(This corresponds to green light)

Problem 2.9

The threshold frequency v_0 for a metal is 7.0×10^{14} s^{-1}. Calculate the kinetic energy of an electron emitted when radiation of frequency $v = 1.0 \times 10^{15}$ s^{-1} hits the metal.

Solution

According to Einstein's equation

Kinetic energy = $\frac{1}{2} m_e v^2 = h(v - v_0)$

$= (6.626 \times 10^{-34} \text{ J s}) (1.0 \times 10^{15} \text{ s}^{-1} - 7.0 \times 10^{14} \text{ s}^{-1})$

$= (6.626 \times 10^{-34} \text{ J s}) (10.0 \times 10^{14} \text{ s}^{-1} - 7.0 \times 10^{14} \text{ s}^{-1})$

$= (6.626 \times 10^{-34} \text{ J s}) \times (3.0 \times 10^{14} \text{ s}^{-1})$

$= 1.988 \times 10^{-19}$ J

2.3.3 Evidence for the quantized* Electronic Energy Levels: Atomic spectra

The speed of light depends upon the nature of the medium through which it passes. As a result, the beam of light is deviated or refracted from its original path as it passes from one medium to another. It is observed that when a ray of white light is passed through a prism, the wave with shorter wavelength bends more than the one with a longer wavelength. Since

ordinary white light consists of waves with all the wavelengths in the visible range, a ray of white light is spread out into a series of coloured bands called **spectrum**. The light of red colour which has longest wavelength is deviated the least while the violet light, which has shortest wavelength is deviated the most. The spectrum of white light, that we can see, ranges from violet at 7.50×10^{14} Hz to red at 4×10^{14} Hz. Such a spectrum is called **continuous spectrum.** Continuous because violet merges into blue, blue into green and so on. A similar spectrum is produced when a rainbow forms in the sky. Remember that visible light is just a small portion of the electromagnetic radiation (Fig.2.7). When electromagnetic radiation interacts with matter, atoms and molecules may absorb energy and reach to a higher energy state. With higher energy, these are in an unstable state. For returning to their normal (more stable, lower energy states) energy state, the atoms and molecules emit radiations in various regions of the electromagnetic spectrum.

Emission and Absorption Spectra

The spectrum of radiation emitted by a substance that has absorbed energy is called an **emission spectrum**. Atoms, molecules or ions that have absorbed radiation are said to be **"excited"**. To produce an emission spectrum, energy is supplied to a sample by heating it or irradiating it and the wavelength (or frequency) of the radiation emitted, as the sample gives up the absorbed energy, is recorded.

An absorption spectrum is like the photographic negative of an emission spectrum. A continuum of radiation is passed through a sample which absorbs radiation of certain wavelengths. The missing wavelength which corresponds to the radiation absorbed by the matter, leave dark spaces in the bright continuous spectrum.

The study of emission or absorption spectra is referred to as **spectroscopy**. The spectrum of the visible light, as discussed above,

was continuous as all wavelengths (red to violet) of the visible light are represented in the spectra. The emission spectra of atoms in the gas phase, on the other hand, do not show a continuous spread of wavelength from red to violet, rather they emit light only at specific wavelengths with dark spaces between them. Such spectra are called **line spectra** or **atomic spectra** because the emitted radiation is identified by the appearance of bright lines in the spectra (Fig. 2.10 page 45).

Line emission spectra are of great interest in the study of electronic structure. Each element has a unique line emission spectrum. The characteristic lines in atomic spectra can be used in chemical analysis to identify unknown atoms in the same way as fingerprints are used to identify people. The exact matching of lines of the emission spectrum of the atoms of a known element with the lines from an unknown sample quickly establishes the identity of the latter, German chemist, Robert Bunsen (1811-1899) was one of the first investigators to use line spectra to identify elements.

Elements like rubidium (Rb), caesium (Cs) thallium (Tl), indium (In), gallium (Ga) and scandium (Sc) were discovered when their minerals were analysed by spectroscopic methods. The element helium (He) was discovered in the sun by spectroscopic method.

Line Spectrum of Hydrogen

When an electric discharge is passed through gaseous hydrogen, the H_2 molecules dissociate and the energetically excited hydrogen atoms produced emit electromagnetic radiation of discrete frequencies. The hydrogen spectrum consists of several series of lines named after their discoverers. Balmer showed in 1885 on the basis of experimental observations that if spectral lines are expressed in terms of wavenumber ($\bar{\nu}$), then the visible lines of the hydrogen spectrum obey the following

formula:

* *The restriction of any property to discrete values is called quantization.*

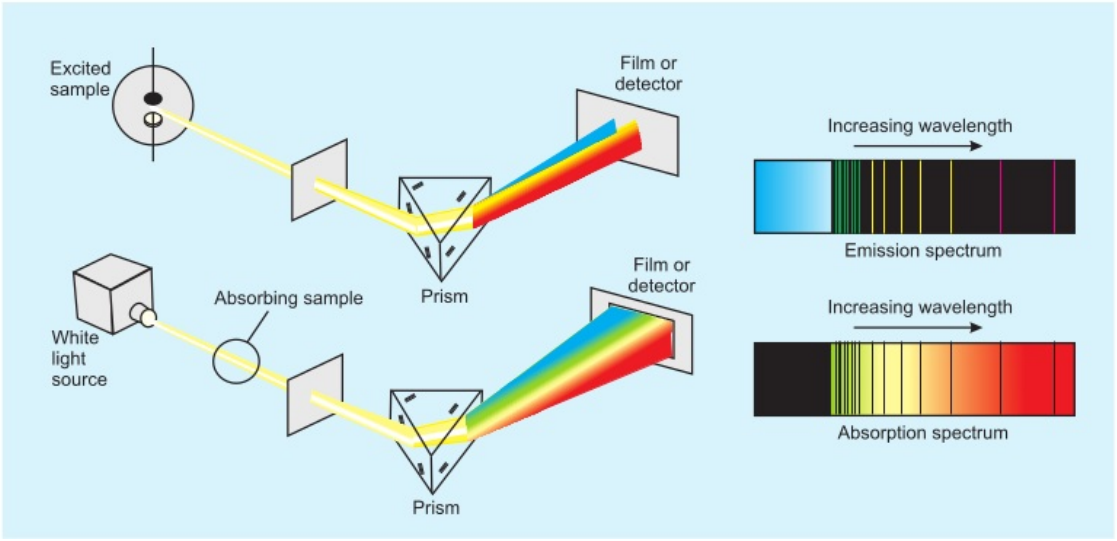


Fig. 2.10 (a) Atomic emission. *The light emitted by a sample of excited hydrogen atoms (or any other element) can be passed through a prism and separated into certain discrete wavelengths. Thus an emission spectrum, which is a photographic recording of the separated wavelengths is called as line spectrum. Any sample of reasonable size contains an enormous number of atoms. Although a single atom can be in only one excited state at a time, the collection of atoms contains all possible excited states. The light emitted as these atoms fall to lower energy states is responsible for the spectrum.* ***(b) Atomic absorption.*** *When white light is passed through unexcited atomic hydrogen and then through a slit and prism, the transmitted light is lacking in intensity at the same wavelengths as are emitted in (a) The recorded absorption spectrum is also a line spectrum and the photographic negative of the emission spectrum.*

$$\bar{\nu} = 109{,}677 \left(\frac{1}{2^2} - \frac{1}{n^2} \right) \text{cm}^{-1} \qquad (2.8)$$

where n is an integer equal to or greater than 3 (i.e., n = 3,4,5,....)

The series of lines described by this formula are called the **Balmer series**. The Balmer series of lines are the only lines in the hydrogen spectrum which appear in the visible region

of the electromagnetic spectrum. The Swedish spectroscopist, Johannes Rydberg, noted that all series of lines in the hydrogen spectrum could be described by the following
expression :

$$\bar{\nu} = 109{,}677 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \text{ cm}^{-1} \qquad (2.9)$$

where n_1=1,2.....

$n_2 = n_1 + 1, n_1 + 2$.....

The value 109,677 cm^{-1} is called the **Rydberg constant** for hydrogen. The first five series of lines that correspond to n_1 = 1, 2, 3, 4, 5 are known as Lyman, Balmer, Paschen, Bracket and Pfund series, respectively, Table 2.3 shows these series of transitions in the hydrogen spectrum. Fig 2.11 (page, 46) shows the Lyman, Balmer and Paschen series of transitions for hydrogen atom.

Table 2.3 The Spectral Lines for Atomic Hydrogen

Series	n_1	n_2	Spectral Region
Lyman	1	2,3....	Ultraviolet
Balmer	2	3,4....	Visible
Paschen	3	4,5....	Infrared
Brackett	4	5,6....	Infrared
Pfund	5	6,7....	Infrared

Of all the elements, hydrogen atom has the simplest line spectrum. Line spectrum becomes more and more complex for heavier atom. There are, however, certain features which are common to all line spectra, i.e., (i) line spectrum of element is unique and (ii) there is regularity in the line

spectrum of each element. The questions which arise are: What are the reasons for these similarities? Is it something to do with the electronic structure of atoms? These are the questions need to be answered. We shall find later that the answers to these questions provide the key in understanding electronic structure of these elements.

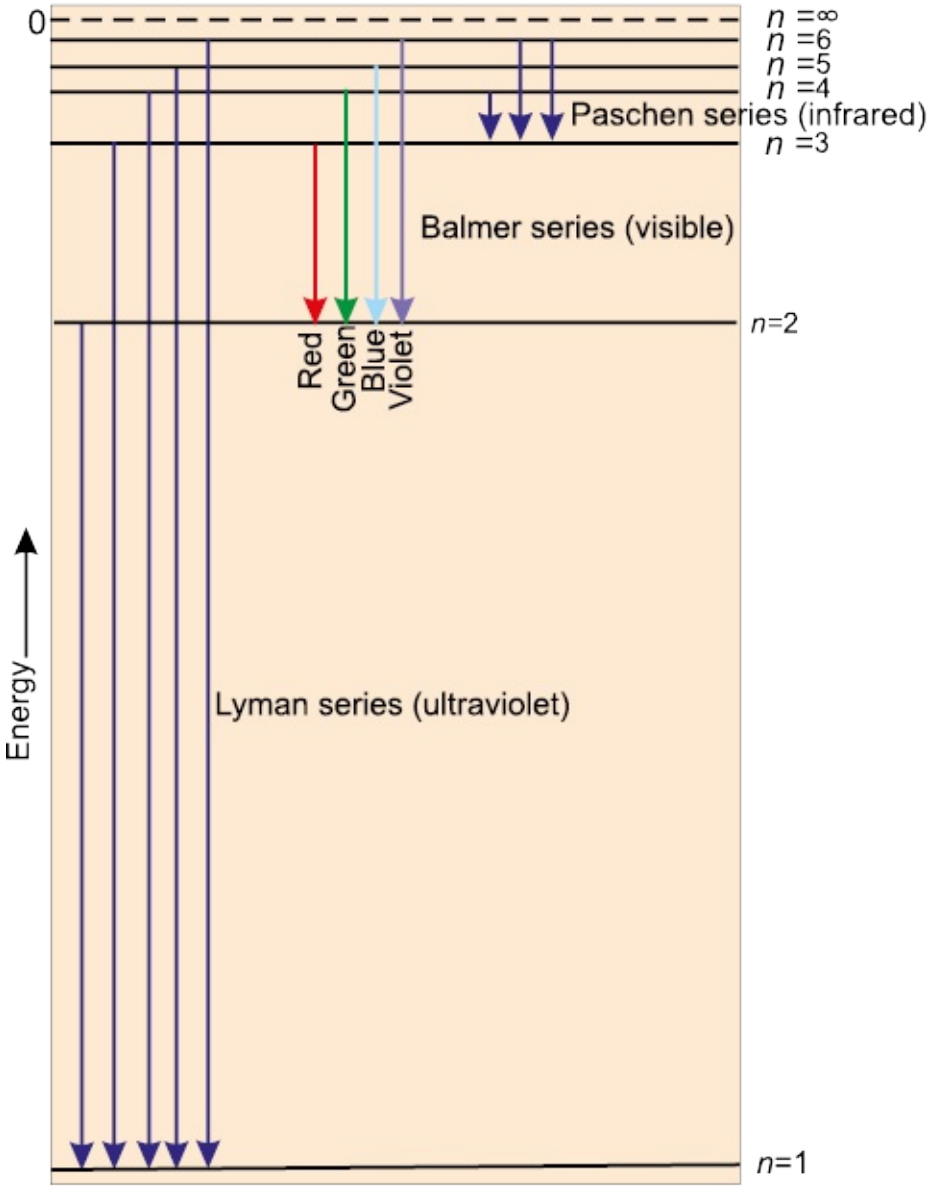


Fig. 2.11 Transitions of the electron in the hydrogen atom (The diagram shows the Lyman, Balmer and Paschen series of transitions)

2.4 Bohr's Model for Hydrogen Atom

Neils Bohr (1913) was the first to explain quantitatively the general features of the structure of hydrogen atom and its spectrum. He used Planck's concept of quantisation of energy. Though the theory is not the modern quantum mechanics, it can still be used to rationalize many points in the atomic structure and spectra. Bohr's model for hydrogen atom is based on the following postulates:

i) The electron in the hydrogen atom can move around the nucleus in a circular path of fixed radius and energy. These paths are called **orbits**, stationary states or allowed energy states. These orbits are arranged concentrically around the nucleus.

ii) The energy of an electron in the orbit does not change with time. However, the electron will move from a lower stationary state to a higher stationary state when required amount of energy is absorbed by the electron or energy is emitted when electron moves from higher stationary state to lower stationary state (equation 2.16). The energy change does not take place in a continuous manner.

Angular Momentum

Just as linear momentum is the product of mass (m) and linear velocity (v), angular momentum is the product of moment of inertia (I) and angular velocity (ω). For an electron of mass m_e, moving in a circular path of radius r around the nucleus,

angular momentum = I × ω

Since $I = m_e r^2$, and ω = v/r where v is the linear velocity,

∴angular momentum = $m_e r^2 \times v/r = m_e vr$

iii) The frequency of radiation absorbed or emitted when transition occurs between two stationary states that differ in energy by ΔE, is given by:

$$\nu = \frac{\Delta E}{h} = \frac{E_2 - E_1}{h} \qquad (2.10)$$

Where E_1 and E_2 are the energies of the lower and higher allowed energy states respectively. This expression is commonly known as Bohr's frequency rule.

iv) The angular momentum of an electron is quantised. In a given stationary state it can be expressed as in equation (2.11)

$$m_e v r = n.\frac{h}{2\pi} \quad n = 1,2,3..... \qquad (2.11)$$

Where m_e is the mass of electron, v is the velocity and r is the radius of the orbit in which electron is moving.

Thus an electron can move only in those orbits for which its angular momentum is integral multiple of h/2π. That means angular momentum is quantised. Radiation is emitted or obsorbed only when transition of electron takes place from one quantised value of angular momentum to another. Therefore, Maxwell's electromagnetic theory does not apply here that is why only certain fixed orbits are allowed.

The details regarding the derivation of energies of the stationary states used by Bohr, are quite complicated and will be discussed in higher classes. However, according to Bohr's theory for hydrogen atom:

a) The stationary states for electron are numbered n = 1,2,3..... These integral numbers (Section 2.6.2) are known as **Principal quantum numbers**.

b) The radii of the stationary states are expressed as: $r_n = n^2 a_0$ (2.12)

where a_0 = 52.9 pm. Thus the radius of the first stationary state, called the **Bohr orbit**, is 52.9 pm. Normally the electron in the hydrogen atom is found in this orbit (that is n=1). As n increases the value of r will increase. In other words the electron will be present away from the nucleus.

c) The most important property associated with the electron, is the energy of its stationary state. It is given by the expression.

$$E_n = -R_H\left(\frac{1}{n^2}\right) \qquad n = 1,2,3.... \qquad (2.13)$$

where R_H is called **Rydberg constant** and its value is 2.18×10^{-18} J. The energy of the lowest state, also called as the ground state, is $E_1 = -2.18\times10^{-18}\left(\frac{1}{1^2}\right) = -2.18\times10^{-18}$ J. The energy of the stationary state for n = 2, will be : $E_2 = -2.18\times10^{-18}$J $\left(\frac{1}{2^2}\right) = -0.545\times10^{-18}$ J. Fig. 2.11 depicts the energies of different stationary states or energy levels of hydrogen atom. This representation is called an energy level diagram.



Niels Bohr

(1885–1962)

Niels Bohr, a Danish physicist received his Ph.D. from the University of Copenhagen in 1911. He then spent a year with J.J. Thomson and Ernest Rutherford in England. In 1913, he returned to Copenhagen where he remained for the rest of his life. In 1920 he was named Director of the Institute of theoretical Physics. After first World War, Bohr worked energetically for peaceful uses of atomic energy. He received the first Atoms for Peace award in 1957. Bohr was awarded the Nobel Prize in Physics in 1922.

When the electron is free from the influence of nucleus, the energy is taken as zero. The electron in this situation is associated with the

stationary state of Principal Quantum number = n = ∞ and is called as ionized hydrogen atom. When the electron is attracted by the nucleus and is present in orbit n, the energy is emitted and its energy is lowered. That is the reason for the presence of negative sign in equation (2.13) and depicts its stability relative to the reference state of zero energy and n = ∞.

What does the negative electronic energy (En) for hydrogen atom mean?

The energy of the electron in a hydrogen atom has a negative sign for all possible orbits (eq. 2.13). What does this negative sign convey? This negative sign means that the energy of the electron in the atom is lower than the energy of a free electron at rest. A free electron at rest is an electron that is infinitely far away from the nucleus and is assigned the energy value of zero. Mathematically, this corresponds to setting n equal to infinity in the equation (2.13) so that E∞=0. As the electron gets closer to the nucleus (as n decreases), En becomes larger in absolute value and more and more negative. The most negative energy value is given by n=1 which corresponds to the most stable orbit. We call this the ground state.

d) Bohr's theory can also be applied to the ions containing only one electron, similar to that present in hydrogen atom. For example, He^{+} Li^{2+}, Be^{3+} and so on. The energies of the stationary states associated with these kinds of ions (also known as hydrogen like species) are given by the expression.

$$E_n = -2.18 \times 10^{-18} \left(\frac{Z^2}{n^2}\right) \text{J} \qquad (2.14)$$

and radii by the expression

$$r_n = \frac{52.9(n^2)}{Z} \text{pm} \qquad (2.15)$$

where Z is the atomic number and has values 2,3 for the helium and lithium atoms respectively. From the above equations, it is evident that

the value of energy becomes more negative and that of radius becomes smaller with increase of Z . This means that electron will be tightly bound to the nucleus.

e) It is also possible to calculate the velocities of electrons moving in these orbits. Although the precise equation is not given here, qualitatively the magnitude of velocity of electron increases with increase of positive charge on the nucleus and decreases with increase of principal quantum number.

2.4.1 Explanation of Line Spectrum of Hydrogen

Line spectrum observed in case of hydrogen atom, as mentioned in section 2.3.3, can be explained quantitatively using Bohr's model. According to assumption 2, radiation (energy) is absorbed if the electron moves from the orbit of smaller Principal quantum number to the orbit of higher Principal quantum number, whereas the radiation (energy) is emitted if the electron moves from higher orbit to lower orbit. The energy gap between the two orbits is given by equation (2.16)

$\Delta E = E_f - E_i$ (2.16)

Combining equations (2.13) and (2.16)

$$\Delta E = \left(-\frac{R_H}{n_f^2}\right) - \left(-\frac{R_H}{n_i^2}\right)$$ (where n_i and n_f stand for initial orbit and final orbits)

$$\Delta E = R_H\left(\frac{1}{n_i^2} - \frac{1}{n_f^2}\right) = 2.18 \times 10^{-18} J\left(\frac{1}{n_i^2} - \frac{1}{n_f^2}\right) \quad (2,17)$$

The frequency (v) associated with the absorption and emission of the photon can be evaluated by using equation (2.18)

$$\nu = \frac{\Delta E}{h} = \frac{R_H}{h}\left(\frac{1}{n_i^2} - \frac{1}{n_f^2}\right)$$

$$= \frac{2.18 \times 10^{-18}\,J}{6.626 \times 10^{-34}\,Js}\left(\frac{1}{n_i^2} - \frac{1}{n_f^2}\right) \qquad (2.18)$$

$$= 3.29 \times 10^{15}\left(\frac{1}{n_i^2} - \frac{1}{n_f^2}\right) Hz \qquad (2.19)$$

and in terms of wavenumbers ($\bar{\nu}$)

$$\bar{\nu} = \frac{\nu}{c} = \frac{R_H}{hc}\left(\frac{1}{n_i^2} - \frac{1}{n_f^2}\right) \qquad (2.20)$$

$$= \frac{3.29 \times 10^{15}\,s^{-1}}{3 \times 10^{8}\,m\,s^{-s}}\left(\frac{1}{n_i^2} - \frac{1}{n_f^2}\right)$$

$$= 1.09677 \times 10^{7}\left(\frac{1}{n_i^2} - \frac{1}{n_f^2}\right) m^{-1} \qquad (2.21)$$

In case of absorption spectrum, $n_f > n_i$ and the term in the parenthesis is positive and energy is absorbed. On the other hand in case of emission spectrum $n_i > n_f$, Δ E is negative and energy is released.

The expression (2.17) is similar to that used by Rydberg (2.9) derived empirically using the experimental data available at that time. Further, each spectral line, whether in absorption or emission spectrum, can be associated to the particular transition in hydrogen atom. In case of large number of hydrogen atoms, different possible transitions can be observed and thus leading to large number of spectral lines. The brightness or intensity of spectral lines depends upon the number of photons of same wavelength or frequency absorbed or emitted.

Problem 2.10

What are the frequency and wavelength of a photon emitted during a transition from n = 5 state to the n = 2 state in the hydrogen atom?

Solution

Since n_i = 5 and n_f = 2, this transition gives rise to a spectral line in the visible region of the

Balmer series. From equation (2.17)

$$\Delta E = 2.18\times10^{-18}\,\text{J}\left[\frac{1}{5^2}-\frac{1}{2^2}\right]$$
$$= -4.58\times10^{-19}\,\text{J}$$

It is an emission energy

The frequency of the photon (taking

energy in terms of magnitude) is given by

$$\nu = \frac{\Delta E}{h}$$
$$= \frac{4.58\times10^{-19}\,\text{J}}{6.626\times10^{-34}\,\text{J s}}$$
$$= 6.91\times10^{14}\,\text{Hz}$$
$$\lambda = \frac{c}{\nu} = \frac{3.0\times10^{8}\,\text{m s}^{-1}}{6.91\times10^{14}\,\text{Hz}} = 434\ \text{nm}$$

Problem 2.11

Calculate the energy associated with the first orbit of He^+. What is the radius of this orbit?

Solution

$$E_n = -\frac{(2.18\times10^{-18}\,\text{J})Z^2}{n^2}\ \text{atom}^{-1}$$

For He^+, $n = 1$, $Z = 2$

$$E_1 = -\frac{(2.18\times10^{-18}\,\text{J})(2^2)}{1^2} = -8.72\times10^{-18}\,\text{J}$$

The radius of the orbit is given by equation (2.15)

$$r_n = \frac{(0.0529\ \text{nm})n^2}{Z}$$

Since $n = 1$, and $Z = 2$

$$r_n = \frac{(0.0529\ \text{nm})1^2}{2} = 0.02645\ \text{nm}$$

2.4.2 Limitations of Bohr's Model

Bohr's model of the hydrogen atom was no doubt an improvement over Rutherford's nuclear model, as it could account for the stability and line spectra of hydrogen atom and hydrogen like ions (for example, He^+, Li^{2+},

Be^{3+}, and so on). However, Bohr's model was too simple to account for the following points.

i) It fails to account for the finer details (doublet, that is two closely spaced lines) of the hydrogen atom spectrum observed by using sophisticated spectroscopic techniques. This model is also unable to explain the spectrum of atoms other than hydrogen, for example, helium atom which possesses only two electrons. Further, Bohr's theory was also unable to explain the splitting of spectral lines in the presence of magnetic field (Zeeman effect) or an electric field (Stark effect).

ii) It could not explain the ability of atoms to form molecules by chemical bonds.

In other words, taking into account the points mentioned above, one needs a better theory which can explain the salient features of the structure of complex atoms.

2.5 Towards Quantum Mechanical Model of the Atom

In view of the shortcoming of the Bohr's model, attempts were made to develop a more suitable and general model for atoms. Two important developments which contributed significantly in the formulation of such a model were :

1. Dual behaviour of matter,
2. Heisenberg uncertainty principle.

2.5.1 Dual Behaviour of Matter

The French physicist, de Broglie, in 1924 proposed that matter, like radiation, should also exhibit dual behaviour i.e., both particle and wavelike properties. This means that just as the photon has momentum as well as wavelength, electrons should also have momentum as well as wavelength, de Broglie, from this analogy, gave the following relation between wavelength (λ) and momentum (p) of a material particle.



Louis de Broglie (1892 – 1987)

Louis de Broglie, a French physicist, studied history as an undergraduate in the early 1910's. His interest turned to science as a result of his assignment to radio communications in World War I. He received his Dr. Sc. from the University of Paris in 1924. He was professor of theoretical physics at the University of Paris from 1932 untill his retirement in 1962. He was awarded the Nobel Prize in Physics in 1929.

$$\lambda = \frac{h}{mv} = \frac{h}{p} \qquad (2.22)$$

where m is the mass of the particle, v its velocity and p its momentum. de Broglie's prediction was confirmed experimentally when it was found that an electron beam undergoes diffraction, a phenomenon characteristic of waves. This fact has been put to use in making an electron microscope, which is based on the wavelike behaviour of electrons just as an ordinary microscope utilises the wave nature of light. An electron microscope is a powerful tool in modern scientific research because it achieves a magnification of about 15 million times.

It needs to be noted that according to de Broglie, every object in motion has a wave character. The wavelengths associated with ordinary objects are so short (because of their large masses) that their wave properties cannot be detected. The wavelengths associated with electrons and

other subatomic particles (with very small mass) can however be detected experimentally. Results obtained from the following problems prove these points qualitatively.

Problem 2.12

What will be the wavelength of a ball of mass 0.1 kg moving with a velocity of 10 m s^{-1} ?

Solution

According to de Brogile equation (2.22)

$$\lambda = \frac{h}{mv} = \frac{(6.626\times10^{-34}\,\text{Js})}{(0.1\,\text{kg})(10\ \text{m s}^{-1})}$$

= 6.626 × 10^{-34} m (J = kg m^2 s^{-2})

Problem 2.13

The mass of an electron is 9.1×10^{-31} kg. If its K.E. is 3.0×10^{-25} J, calculate its wavelength.

Solution

Since K. E. = ½ mv^2

$$v = \left(\frac{2\text{K.E.}}{m}\right)^{1/2} = \left(\frac{2\times3.0\times10^{-25}\,\text{kg m}^2\text{s}^{-2}}{9.1\times10^{-31}\,\text{kg}}\right)^{1/2}$$

$$= 812\ \text{m s}^{-1}$$

$$\lambda = \frac{h}{mv} = \frac{6.626\times10^{-34}\,\text{Js}}{(9.1\times10^{-31}\,\text{kg})(812\ \text{m s}^{-1})}$$

$$= 8967\times10^{-10}\ \text{m} = 896.7\ \text{nm}$$

Problem 2.14

Calculate the mass of a photon with wavelength 3.6 Å.

Solution

λ = 3.6 Å = 3.6 × 10^{-10} m

Velocity of photon = velocity of light

$$m = \frac{h}{\lambda v} = \frac{6.626\times10^{-34}\,\text{Js}}{(3.6\times10^{-10}\,\text{m})(3\times10^{8}\ \text{m s}^{-1})}$$

$= 6.135 \times 10^{-29}$ kg

2.5.2 Heisenberg's Uncertainty Principle

Werner Heisenberg a German physicist in 1927, stated uncertainty principle which is the consequence of dual behaviour of matter and radiation. **It states that it is impossible to determine simultaneously, the exact position and exact momentum (or velocity) of an electron.** Mathematically, it can be given as in equation (2.23).

$$\Delta x \times \Delta p_x \geq \frac{h}{4\pi} \qquad (2.23)$$

$$\text{or } \Delta x \times \Delta(mv_x) \geq \frac{h}{4\pi}$$

$$\text{or } \Delta x \times \Delta v_x \geq \frac{h}{4\pi m}$$

where Δx is the uncertainty in position and Δpx (or Δv_x) is the uncertainty in momentum (or velocity) of the particle. If the position of the electron is known with high degree of accuracy (Δx is small), then the velocity of the electron will be uncertain [$\Delta(v_x)$ is large]. On the other hand, if the velocity of the electron is known precisely ($\Delta(vx$) is small), then the position of the electron will be uncertain
(Δx will be large). Thus, if we carry out some physical measurements on the electron's position or velocity, the outcome will always depict a fuzzy or blur picture.

The uncertainty principle can be best understood with the help of an example. Suppose you are asked to measure the thickness of a sheet of paper with an unmarked metrestick. Obviously, the results obtained would be extremely inaccurate and meaningless, In order to obtain any accuracy, you should use an instrument graduated in units smaller than the thickness of a sheet of the paper. Analogously, in order to determine

the position of an electron, we must use a meterstick calibrated in units of smaller than the dimensions of electron (keep in mind that an electron is considered as a point charge and is therefore, dimensionless). To observe an electron, we can illuminate it with “light” or electromagnetic radiation. The “light” used must have a wavelength smaller than the dimensions of an electron. The high momentum photons of such light $\left(p=\frac{h}{\lambda}\right)$ would change the energy of electrons by collisions. In this process we, no doubt, would be able to calculate the position of the electron, but we would know very little about the velocity of the electron after the collision.

Significance of Uncertainty Principle

One of the important implications of the Heisenberg Uncertainty Principle is that **it rules out existence of definite paths or trajectories of electrons and other similar particles.** The trajectory of an object is determined by its location and velocity at various moments. If we know where a body is at a particular instant and if we also know its velocity and the forces acting on it at that instant, we can tell where the body would be sometime later. We, therefore, conclude that the position of an object and its velocity fix its trajectory. Since for a sub-atomic object such as an electron, it is not possible simultaneously to determine the position and velocity at any given instant to an arbitrary degree of precision, it is not possible to talk of the trajectory of an electron.

The effect of Heisenberg Uncertainty Principle is significant only for motion of microscopic objects and is negligible for that of macroscopic objects. This can be seen from the following examples.



Werner Heisenberg (1901 – 1976) Werner Heisenberg (1901 – 1976) received his Ph.D. in physics from the University of Munich in 1923. He then spent a year working with Max Born at Gottingen and three years with Niels Bohr in Copenhagen. He was professor of physics at the University of Leipzig from 1927 to 1941. During World War II, Heisenberg was in charge of German research on the atomic bomb. After the war he was named director of Max Planck Institute for physics in Gottingen. He was also accomplished mountain climber. Heisenberg was awarded the Nobel Prize in Physics in 1932.

If uncertainty principle is applied to an object of mass, say about a milligram (10–6 kg), then

$$\Delta v.\Delta x = \frac{h}{4\pi.m}$$

$$= \frac{6.626\times10^{-34}\,\mathrm{J\,s}}{4\times3.1416\times10^{-6}\,\mathrm{kg}} \approx 10^{-28}\mathrm{m^{2}s^{-1}}$$

The value of $\Delta v\Delta x$ obtained is extremely small and is insignificant. Therefore, one may say that **in dealing with milligram-sized or heavier objects, the associated uncertainties are hardly of any real consequence.**

In the case of a microscopic object like an electron on the other hand. $\Delta v.\Delta x$ obtained is much larger and such uncertainties are of real consequence. For example, for an electron whose mass is 9.11×10^{-31} kg., according to Heisenberg uncertainty principle

$$\Delta v.\Delta x = \frac{h}{4\pi m}$$

$$= \frac{6.626\times10^{-34}\ \text{Js}}{4\times 3.1416\times 9.11\times10^{-31}\ \text{kg}}$$

$$= 10^{-4}\text{m}^2\text{s}^{-1}$$

It, therefore, means that if one tries to find the exact location of the electron, say to an uncertainty of only 10^{-8} m, then the uncertainty Δv in velocity would be

which is so large that the classical picture of electrons moving in Bohr's orbits (fixed) cannot hold good. **It, therefore, means that the precise statements of the position and momentum of electrons have to be replaced by the statements of probability, that the electron has at a given position and momentum. This is what happens in the quantum mechanical model of atom.**

Problem 2.15

A microscope using suitable photons is employed to locate an electron in an atom within a distance of 0.1 Å. What is the uncertainty involved in the measurement of its velocity?

Solution

$$\Delta x\,\Delta p = \frac{h}{4\pi} \text{ or } \Delta x m\Delta v = \frac{h}{4\pi}$$

$$\Delta v = \frac{h}{4\pi\Delta x m}$$

$$\Delta v = \frac{6.626\times10^{-34}\ \text{Js}}{4\times3.14\times0.1\times10^{-10}\text{m}\times9.11\times10^{-31}\ \text{kg}}$$

$= 0.579\times10^{7}$ m s^{-1} (1J = 1 kg m^2 s^{-2})

$= 5.79\times10^{6}$ m s^{-1}

Problem 2.16

A golf ball has a mass of 40g, and a speed of 45 m/s. If the speed can be measured within

accuracy of 2%, calculate the uncertainty in the position.

Solution

The uncertainty in the speed is 2%, i.e.,

$$45 \quad \frac{2}{100} = 0.9\,\mathrm{m\,s^{-1}}$$

Using the equation (2.22)

$$\Delta x = \frac{h}{4\pi m \Delta v}$$

$$= \frac{6.626 \times 10^{-34}\ \mathrm{Js}}{4 \times 3.14 \times 40\mathrm{g} \times 10^{-3}\ \mathrm{kg\,g^{-1}}\,(0.9\,\mathrm{m\,s^{-1}})}$$

$= 1.46 \times 10^{-33}$ m

This is nearly ~ 10^{18} times smaller than the diameter of a typical atomic nucleus. As mentioned earlier for large particles, the uncertainty principle sets no meaningful limit to the precision of measurements.

Reasons for the Failure of the Bohr Model

One can now understand the reasons for the failure of the Bohr model. In Bohr model, an electron is regarded as a charged particle moving in well defined circular orbits about the nucleus. The wave character of the electron is not considered in Bohr model. Further, an orbit is a clearly defined path and this path can completely be defined only if both the position and the velocity of the electron are known exactly at the same time. This is not possible according to the Heisenberg uncertainty principle. *Bohr model of the hydrogen atom, therefore, not only ignores dual behaviour of matter but also contradicts Heisenberg uncertainty principle*. In view of these inherent weaknesses in the Bohr model, there was no point in extending Bohr model to other atoms. In fact an insight into the structure of the atom was needed which could account for wave-particle duality of matter and be consistent with Heisenberg uncertainty principle. This came with the advent of quantum mechanics.



Erwin Schrödinger

(1887-1961)

Erwin Schrödinger, an Austrian physicist received his Ph.D. in theoretical physics from the University of Vienna in 1910. In 1927 Schrödinger succeeded Max Planck at the University of Berlin at Planck's request. In 1933, Schrödinger left Berlin because of his opposition to Hitler and Nazi policies and returned to Austria in 1936. After the invasion of Austria by Germany, Schrödinger was forcibly removed from his professorship. He then moved to Dublin, Ireland where he remained for seventeen years. Schrödinger shared the Nobel Prize for Physics with P.A.M. Dirac in 1933.

2.6 Quantum Mechanical Model of Atom

Classical mechanics, based on Newton's laws of motion, successfully describes the motion of all macroscopic objects such as a falling stone, orbiting planets etc., which have essentially a particle-like behaviour as shown in the previous section. However it fails when applied to microscopic objects like electrons, atoms, molecules etc. This is mainly because of the fact that classical mechanics ignores the concept of dual behaviour of matter especially for sub-atomic particles and the uncertainty principle. The branch of science that takes into account this dual behaviour of matter is called **quantum mechanics**.

Quantum mechanics is a theoretical science that deals with the study of

the motions of the microscopic objects that have both observable wave like and particle like properties. It specifies the laws of motion that these objects obey. When quantum mechanics is applied to macroscopic objects (for which wave like properties are insignificant) the results are the same as those from the classical mechanics.

Quantum mechanics was developed independently in 1926 by Werner Heisenberg and Erwin Schrödinger. Here, however, we shall be discussing the quantum mechanics which is based on the ideas of wave motion. The fundamental equation of quantum mechanics was developed by Schrödinger and it won him the Nobel Prize in Physics in 1933. This equation which incorporates wave-particle duality of matter as proposed by de Broglie is quite complex and knowledge of higher mathematics is needed to solve it. You will learn its solutions for different systems in higher classes.

For a system (such as an atom or a molecule whose energy does not change with time) the **Schrödinger equation** is written as $\hat{H}\Psi = E\Psi$ where $\hat{H}$ is a mathematical operator called Hamiltonian. Schrödinger gave a recipe of constructing this operator from the expression for the total energy of the system. The total energy of the system takes into account the kinetic energies of all the sub-atomic particles (electrons, nuclei), attractive potential between the electrons and nuclei and repulsive potential among the electrons and nuclei individually. Solution of this equation gives E and ψ.

Hydrogen Atom and the Schrödinger Equation

When Schrödinger equation is solved for hydrogen atom, the solution gives the possible energy levels the electron can occupy and the corresponding wave function(s) (ψ) of the electron associated with each energy level. These quantized energy states and corresponding wave functions which are characterized by a set of three quantum numbers (**principal quantum number** n**, azimuthal quantum number** l **and**

magnetic quantum number ml) arise as a natural consequence in the solution of the Schrödinger equation. When an electron is in any energy state, the wave function corresponding to that energy state contains all information about the electron. The wave function is a mathematical function whose value depends upon the coordinates of the electron in the atom and does not carry any physical meaning. Such wave functions of hydrogen or hydrogen like species with one electron are called **atomic orbitals**. Such wave functions pertaining to one-electron species are called one-electron systems. The probability of finding an electron at a point within an atom is proportional to the $|\psi|^2$ at that point. The quantum mechanical results of the hydrogen atom successfully predict all aspects of the hydrogen atom spectrum including some phenomena that could not be explained by the Bohr model.

Application of Schrödinger equation to multi-electron atoms presents a difficulty: the Schrödinger equation cannot be solved exactly for a multi-electron atom. This difficulty can be overcome by using approximate methods. Such calculations with the aid of modern computers show that orbitals in atoms other than hydrogen do not differ in any radical way from the hydrogen orbitals discussed above. The principal difference lies in the consequence of increased nuclear charge. Because of this all the orbitals are somewhat contracted. Further, as you shall see later (in subsections 2.6.3 and 2.6.4), unlike orbitals of hydrogen or hydrogen like species, whose energies depend only on the quantum number n, the energies of the orbitals in multi-electron atoms depend on quantum numbers n and l.

Important Features of the Quantum Mechanical Model of Atom

Quantum mechanical model of atom is the picture of the structure of the atom, which emerges from the application of the Schrödinger equation to atoms. The following are the

important features of the quantum-mechanical model of atom:

1. The energy of electrons in atoms is quantized (i.e., can only have certain specific values), for example when electrons are bound to the nucleus in atoms.

2. The existence of quantized electronic energy levels is a direct result of the wave like properties of electrons and are allowed solutions of Schrödinger wave equation.

3. Both the exact position and exact velocity of an electron in an atom cannot be determined simultaneously (Heisenberg uncertainty principle). The path of an electron in an atom therefore, can never be determined or known accurately. That is why, as you shall see later on, one talks of only probability of finding the electron at different points in an atom.

4. **An atomic orbital is the wave function ψ for an electron in an atom**. Whenever an electron is described by a wave function, we say that the electron occupies that orbital. Since many such wave functions are possible for an electron, there are many atomic orbitals in an atom. These “one electron orbital wave functions” or orbitals form the basis of the electronic structure of atoms. In each orbital, the electron has a definite energy. An orbital cannot contain more than two electrons. In a multi-electron atom, the electrons are filled in various orbitals in the order of increasing energy. For each electron of a multi-electron atom, there shall, therefore, be an orbital wave function characteristic of the orbital it occupies. All the information about the electron in an atom is stored in its orbital wave function ψ and quantum mechanics makes it possible to extract this information out of ψ.

5. The probability of finding an electron at a point within an atom is proportional to the square of the orbital wave function i.e., $|\psi|^2$ at that point. $|\psi|^2$ is known as **probability density** and is always positive. From the value of $\mathbf{|\psi|^2}$ at different points within an atom, it is possible to predict the region around the nucleus where electron will most probably be found.

2.6.1 Orbitals and Quantum Numbers

A large number of orbitals are possible in an atom. Qualitatively these orbitals can be distinguished by their size, shape and orientation. An orbital of smaller size means there is more chance of finding the electron near the nucleus. Similarly shape and orientation mean that there is more probability of finding the electron along certain directions than along others. Atomic orbitals are precisely distinguished by what are known as quantum numbers. Each orbital is designated by three quantum numbers labelled as n, l and ml.

The principal quantum number 'n' is a positive integer with value of n = 1,2,3..... The principal quantum number determines the size and to large extent the energy of the orbital. For hydrogen atom and hydrogen like species (He^+, Li^{2+}, ... etc.) energy and size of the orbital depends only on 'n'.

The principal quantum number also identifies the **shell**. With the increase in the value of 'n', the number of allowed orbital increases and **are given by 'n^2' All the orbitals of a given value of 'n' constitute a single shell of atom** and are represented by the following letters

n = 1 2 3 4 .....

Shell = K L M N .....

Size of an orbital increases with increase of principal quantum number 'n'. In other words the electron will be located away from the nucleus. Since energy is required in shifting away the negatively charged electron from the positively charged nucleus, the energy of the orbital will increase with increase of n.

Azimuthal quantum number. 'l' is also known as **orbital angular momentum or subsidiary quantum number.** It defines the three-dimensional shape of the orbital. For a given value of n, l can have n values ranging from 0 to n – 1, that is, for a given value of n, the possible value of l are : l = 0, 1, 2, ... (n–1)

For example, when n = 1, value of l is only 0. For n = 2, the possible value of l can be 0 and 1. For n = 3, the possible l values are 0, 1 and 2.

Each shell consists of one or more **sub-shells** or **sub-levels**. The number of sub-shells in a principal shell is equal to the value of n. For example in the first shell (n = 1), there is only one sub-shell which corresponds to l = 0. There are two sub-shells (l = 0, 1) in the second shell (n = 2), three (l = 0, 1, 2) in third shell (n = 3) and so on. Each sub-shell is assigned an azimuthal quantum number (l). Sub-shells corresponding to different values of l are represented by the following symbols.

Value for l : 0 1 2 3 4 5 .....

notation for s p d f g h .....

sub-shell

Table 2.4 shows the permissible values of 'l ' for a given principal quantum number and the corresponding sub-shell notation.

Magnetic orbital quantum number. 'ml' gives information about **the spatial orientation of the orbital with respect to standard set of co-ordinate axis.** For any **sub-shell (defined by 'l' value)** 2l+1 values of ml are possible and these values are given by :

ml = – l, – (l–1), – (l–2)... 0,1... (l–2), (l–1), l

Thus for l = 0, the only permitted value of ml = 0, [2(0)+1 = 1, one s orbital]. For l = 1, ml can be –1, 0 and +1 [2(1)+1 = 3, three p orbitals]. For l = 2, ml = –2, –1, 0, +1 and +2, [2(2)+1 = 5, five d orbitals]. It should be noted that the values of ml are derived from l and that the value of l are derived from n.

Table 2.4 Subshell Notations

n	l	Subshell notation
1	0	$1s$
2	0	$2s$
2	1	$2p$
3	0	$3s$
3	1	$3p$
3	2	$3d$
4	0	$4s$
4	1	$4p$
4	2	$4d$
4	3	$4f$

Each orbital in an atom, therefore, is defined by a set of values for n, l and ml. An orbital described by the quantum numbers
n = 2, l = 1, ml = 0 is an orbital in the p sub-shell of the second shell. The following chart gives the relation between the subshell and the number of orbitals associated with it.

Value of l	0	1	2	3	4	5
Subshell notation	s	p	d	f	g	h
number of orbitals	1	3	5	7	9	11

Electron spin 's' : The three quantum numbers labelling an atomic orbital can be used equally well to define its energy, shape and orientation. But all these quantum numbers are not enough to explain the line spectra observed in the case of multi-electron atoms, that is, some of

the lines actually occur in doublets (two lines closely spaced), triplets (three lines, closely spaced) etc. This suggests the presence of a few more energy levels than predicted by the three quantum numbers.

In 1925, George Uhlenbeck and Samuel Goudsmit proposed the presence of the fourth quantum number known as the **electron spin quantum number (**ms**).** An electron spins around its own axis, much in a similar way as earth spins around its own axis while revolving around the sun. In other words, an electron has, besides charge and mass, intrinsic spin angular quantum number. Spin angular momentum of the electron — a vector quantity, can have two orientations relative to the chosen axis. These two orientations are distinguished by the spin quantum numbers m_s which can take the values of +½ or –½. These are called the **two spin states of the electron** and are normally represented by two arrows, ↑ (spin up) and ↓ (spin down). Two electrons that have different m_s values (one +½ and the other –½) are said to have opposite spins. An orbital cannot hold more than two electrons and these two electrons should have opposite spins.

To sum up, the four quantum numbers provide the following information :

i) n defines the shell, determines the size of the orbital and also to a large extent the energy of the orbital.

ii) There are n subshells in the n^{th} shell. l identifies the subshell and determines the shape of the orbital (see section 2.6.2). There are (2l+1) orbitals of each type in a subshell, that is, one s orbital (l = 0), three p orbitals (l = 1) and five d orbitals (l = 2) per subshell. To some extent l also determines the energy of the orbital in a multi-electron atom.

iii) ml designates the orientation of the orbital. For a given value of l, ml has (2l+1) values, the same as the number of orbitals per subshell. It means that the number of orbitals is equal to the number of ways in

which they are oriented.

iv) m_s refers to orientation of the spin of the electron.

Orbit, orbital and its importance

Orbit and orbital are not synonymous. An orbit, as proposed by Bohr, is a circular path around the nucleus in which an electron moves. A precise description of this path of the electron is impossible according to Heisenberg uncertainty principle. Bohr orbits, therefore, have no real meaning and their existence can never be demonstrated experimentally. An atomic orbital, on the other hand, is a quantum mechanical concept and refers to the one electron wave function ψ in an atom. It is characterized by three quantum numbers (n, l and ml) and its value depends upon the coordinates of the electron. ψ has, by itself, no physical meaning. It is the square of the wave function i.e., $|\psi|^2$ which has a physical meaning. $|\psi|^2$ at any point in an atom gives the value of probability density at that point. Probability density ($|\psi|^2$) is the probability per unit volume and the product of $|\psi|^2$ and a small volume (called a volume element) yields the probability of finding the electron in that volume (the reason for specifying a small volume element is that $|\psi|^2$ varies from one region to another in space but its value can be assumed to be constant within a small volume element). The total probability of finding the electron in a given volume can then be calculated by the sum of all the products of $|\psi|^2$ and the corresponding volume elements. It is thus possible to get the probable distribution of an electron in an orbital.

Problem 2.17

What is the total number of orbitals associated with the principal quantum number n = 3 ?

Solution

For n = 3, the possible values of l are 0, 1 and 2. Thus there is one 3s orbital (n = 3, l = 0 and ml = 0); there are three 3p orbitals (n = 3, l = 1 and ml = –1, 0, +1); there are five 3d orbitals (n = 3, l = 2 and ml = –2, –1, 0, +1+, +2).

Therefore, the total number of orbitals is 1+3+5 = 9

The same value can also be obtained by using the relation; number of orbitals

= n^2, i.e. 3^2 = 9.

Problem 2.18

Using s, p, d, f notations, describe the orbital with the following quantum numbers

(a) n = 2, l = 1, (b) n = 4, l = 0, (c) n = 5,

l = 3, (d) n = 3, l = 2

Solution

	n	l	orbital
a)	2	1	$2p$
b)	4	0	$4s$
c)	5	3	$5f$
d)	3	2	$3d$

2.6.2 Shapes of Atomic Orbitals

The orbital wave function or ψ for an electron in an atom has no physical meaning. It is simply a mathematical function of the coordinates of the electron. However, for different orbitals the plots of corresponding wave functions as a function of r (the distance from the nucleus) are different. Fig. 2.12(a), gives such plots for 1s (n = 1, l = 0) and 2s (n = 2, l = 0) orbitals.

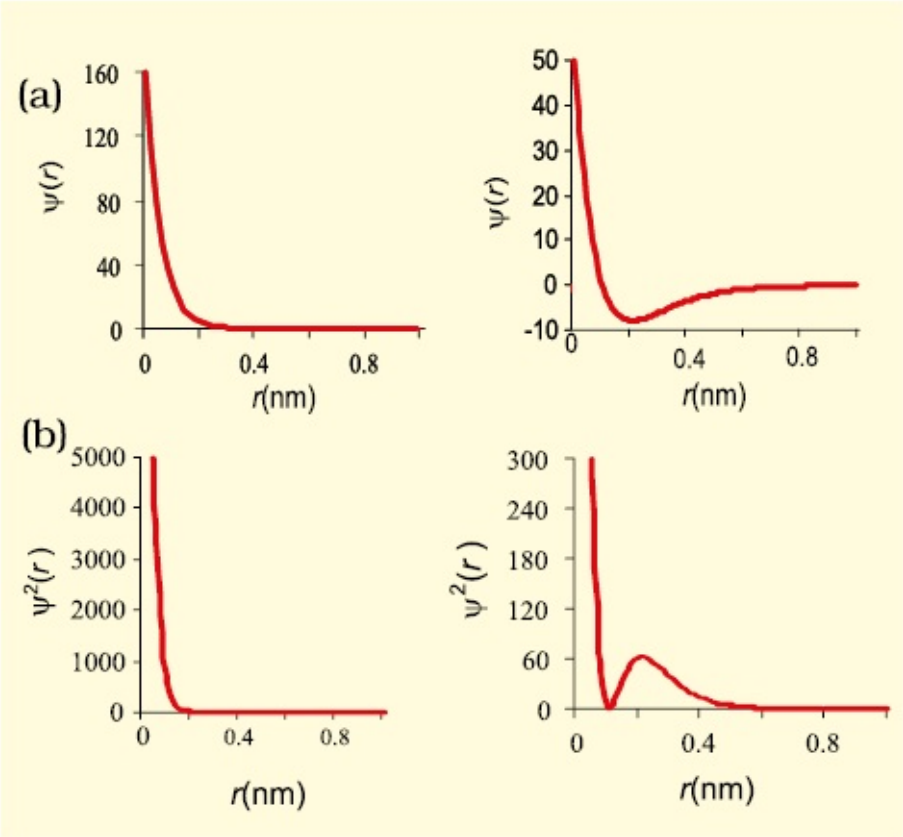


Fig. 2.12 *The plots of (a) the orbital wave function ψ(r); (b) the variation of probability density ψ2(r) as a function of distance r of the electron from the nucleus for 1s and 2s orbitals.*

According to the German physicist, Max Born, the square of the wave function (i.e.,ψ^2) at a point gives the probability density of the electron at that point. The variation of ψ^2 as a function of r for 1s and 2s orbitals is given in Fig. 2.12(b). Here again, you may note that the curves for 1s and 2s orbitals are different.

It may be noted that for 1s orbital the probability density is maximum at the nucleus and it decreases sharply as we move away from it. On the other hand, for 2s orbital the probability density first decreases sharply to zero and again starts increasing. After reaching a small maxima it decreases again and approaches zero as the value of r increases further. The region where this probability density function reduces to zero is called **nodal surfaces** or simply **nodes**. In general, it has been found

that ns-orbital has (n – 1) nodes, that is, number of nodes increases with increase of principal quantum number n. In other words, number of nodes for 2s orbital is one, two for 3s and so on.

These probability density variation can be visualised in terms of charge cloud diagrams [Fig. 2.13(a)]. In these diagrams, the density of the dots in a region represents electron probability density in that region.

Boundary surface diagrams of constant probability density for different orbitals give a fairly good representation of the shapes of the orbitals. In this representation, a boundary surface or contour surface is drawn in space for an orbital on which the value of probability density $|\psi|^2$ is constant. In principle many such boundary surfaces may be possible. However, for a given orbital, only that boundary surface diagram of constant probability density* is taken to be good representation of the shape of the orbital which encloses a region or volume in which the probability of finding the electron is very high, say, 90%. The boundary surface diagram for 1s and 2s orbitals are given in Fig. 2.13(b). One may ask a question : Why do we not draw a boundary surface diagram, which bounds a region in which the probability of finding the electron is, 100 %? The answer to this question is that the probability density $|\psi|^2$ has always some value, howsoever small it may be, at any finite distance from the nucleus. It is therefore, not possible to draw a boundary surface diagram of a rigid size in which the probability of finding the electron is 100%. Boundary surface diagram for a s orbital is actually a sphere centred on the nucleus. In two dimensions, this sphere looks like a circle. It encloses a region in which probability of finding the electron is about 90%.

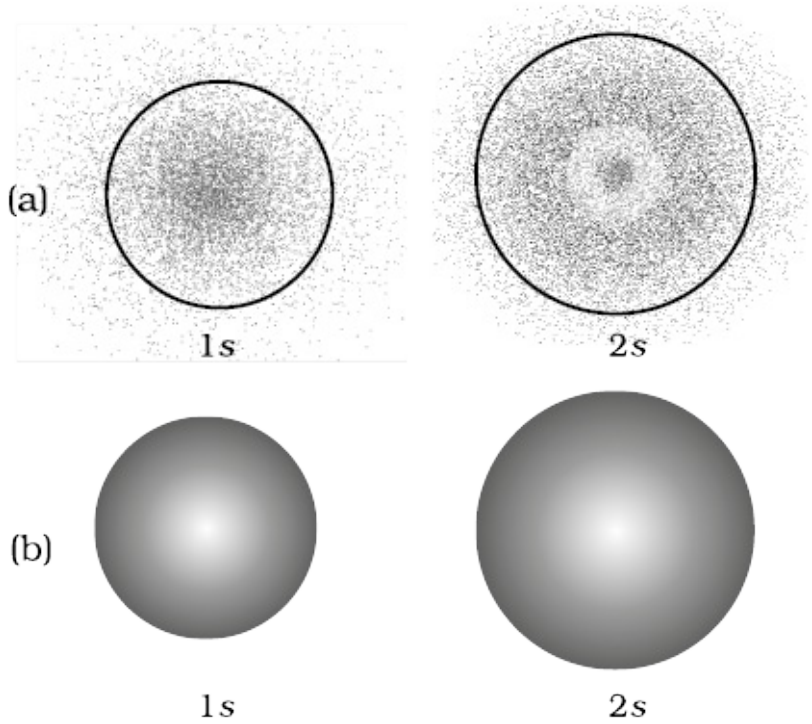


Fig. 2.13 (a) Probability density plots of 1s and 2s atomic orbitals. The density of the dots represents the probability density of finding the electron in that region. (b) Boundary surface diagram for 1s and 2s orbitals.

Thus, we see that 1s and 2s orbitals are spherical in shape. In reality all the s-orbitals are spherically symmetric, that is, the probability of finding the electron at a given distance is equal in all the directions. It is also observed that the size of the s orbital increases with increase in n, that is, 4s > 3s > 2s > 1s and the electron is located further away from the nucleus as the principal quantum number increases.

Boundary surface diagrams for three 2p orbitals (l = 1) are shown in Fig. 2.14. In these diagrams, the nucleus is at the origin. Here, unlike s-orbitals, the boundary surface diagrams are not spherical. Instead each p orbital consists of two sections called lobes that are on either side of the plane that passes through the nucleus. The probability density function is zero on the plane where the two lobes touch each other. The size, shape and energy of the three orbitals are identical. They differ however, in the

way the lobes are oriented. Since the lobes may be considered to lie along the x, y or z axis, they are given the designations 2px, 2py, and 2pz. It should be understood, however, that there is no simple relation between the values of ml (–1, 0 and +1) and the x, y and z directions. For our purpose, it is sufficient to remember that, because there are three possible values of ml, there are, therefore, three p orbitals whose axes are mutually perpendicular. Like s orbitals, p orbitals increase in size and energy with increase in the principal quantum number and hence the order of the energy and size of various p orbitals is 4p > 3p > 2p. Further, like s orbitals, the probability density functions for p-orbital also pass through value zero, besides at zero and infinite distance, as the distance from the nucleus increases. The number of nodes are given by the n –2, that is number of radial node is 1 for 3p orbital, two for 4p orbital and so on.

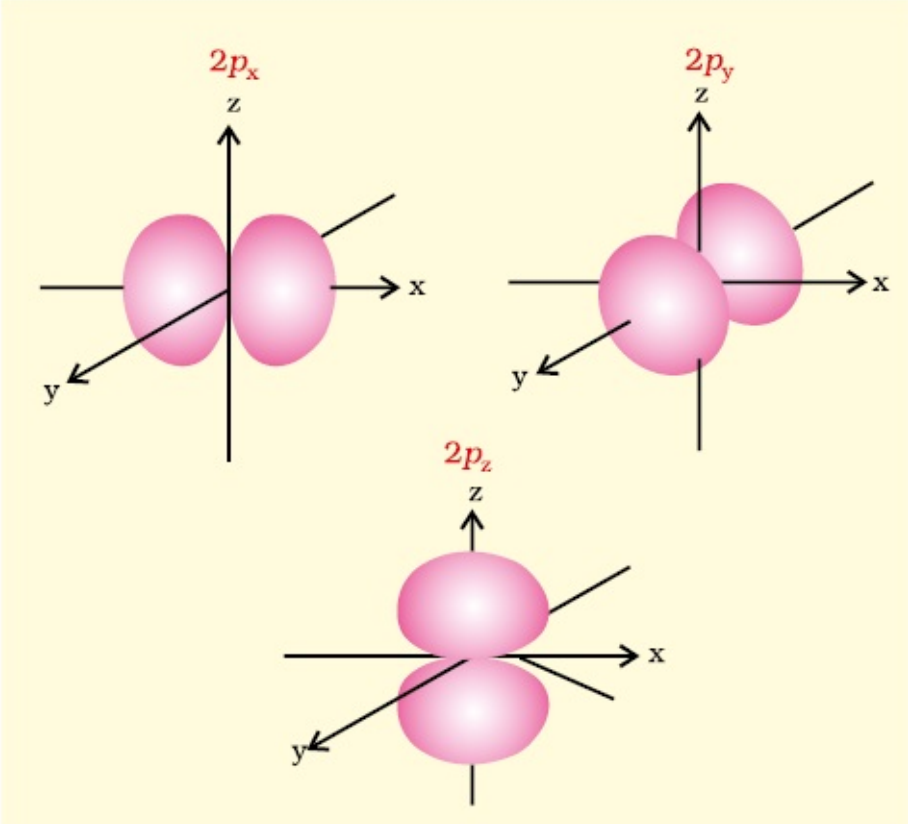


Fig. 2.14 Boundary surface diagrams of the three 2p orbitals.

* *If probability density $|\psi|^2$ is constant on a given surface, $|\psi|$ is also constant over the surface. The boundary surface for $|\psi|^2$ and $|\psi|$ are identical.*

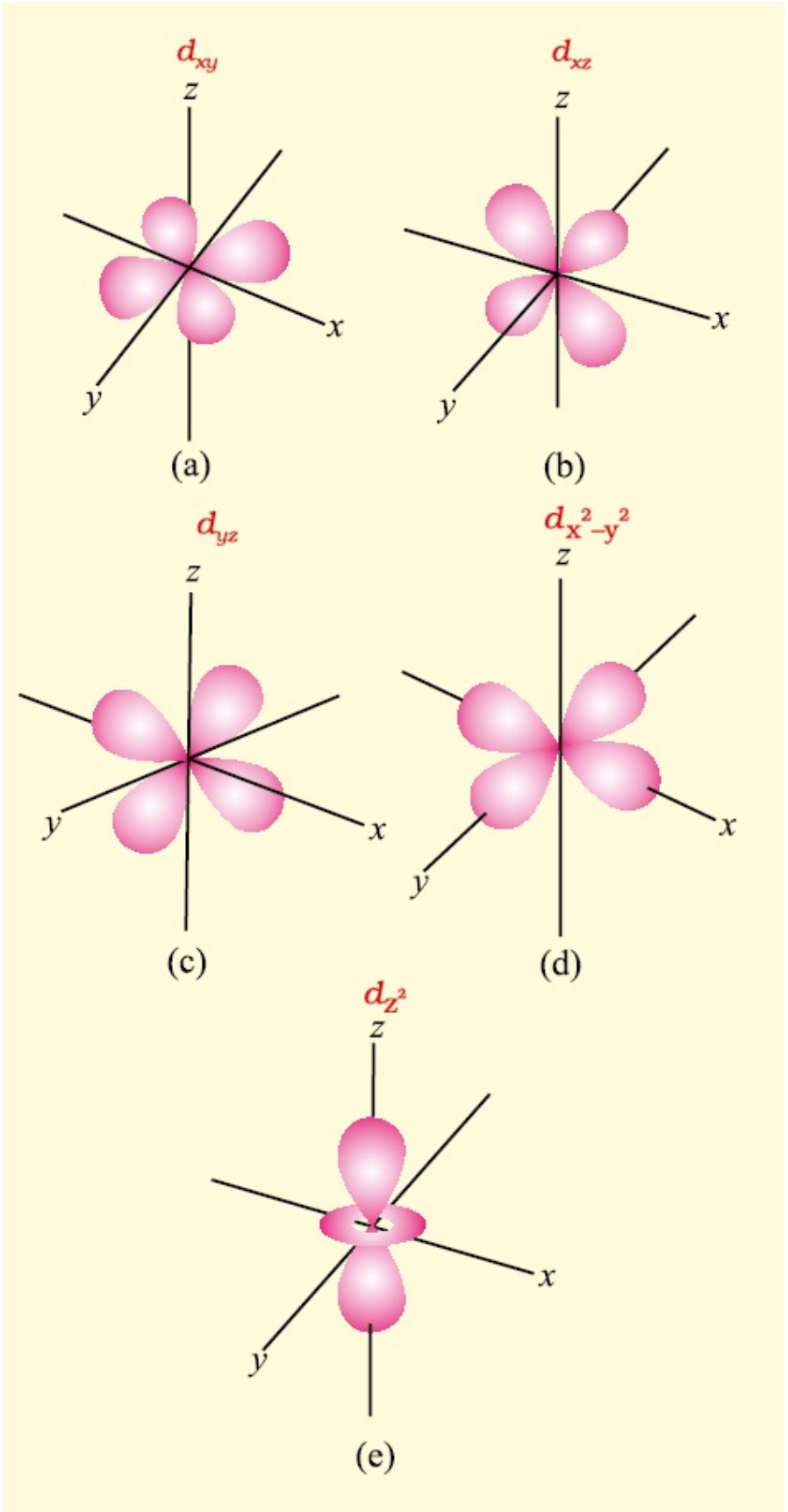

d_{xy}
z
x
y
(a)
d_{xz}
z
x
y
(b)
d_{yz}
z
y
x
(c)
$d_{x^2-y^2}$
z
x
y
(d)
d_{z^2}
z
x
y
(e)

Fig. 2.15 Boundary surface diagrams of the five 3d orbitals.

For l = 2, the orbital is known as d-orbital and the minimum value of principal quantum number (n) has to be 3. as the value of l cannot be greater than n–1. There are five ml values (–2, –1, 0, +1 and +2) for l = 2 and thus there are five d orbitals. The boundary surface diagram of d orbitals are shown in Fig. 2.15.

The five d-orbitals are designated as d_{xy}, d_{yz}, d_{xz}, d_{x2-y2} and d_{z2}. The shapes of the first four d-orbitals are similar to each other, where as that of the fifth one, d_{z2}, is different from others, but all five 3d orbitals are equivalent in energy. The d orbitals for which n is greater than 3 (4d, 5d...) also have shapes similar to 3d orbital, but differ in energy and size.

Besides the radial nodes (i.e., probability density function is zero), the probability density functions for the np and nd orbitals are zero at the plane (s), passing through the nucleus (origin). For example, in case of p_z orbital, xy-plane is a nodal plane, in case of d_{xy} orbital, there are two nodal planes passing through the origin and bisecting the xy plane containing z-axis. These are called angular nodes and number of angular nodes are given by 'l', i.e., one angular node for p orbitals, two angular nodes for 'd' orbitals and so on. **The total number of nodes are given by (**n**–1), i.e.,** sum of l **angular nodes and (**n **–** l **– 1) radial nodes.**

2.6.3 Energies of Orbitals

The energy of an electron in a hydrogen atom is determined solely by the principal quantum number. Thus the energy of the orbitals in hydrogen atom increases as follows :

1s < 2s = 2p < 3s = 3p = 3d <4s = 4p = 4d

= 4f < (2.23)

and is depicted in Fig. 2.16. Although the shapes of 2s and 2p orbitals are different, an electron has the same energy when it is in the 2s orbital as when it is present in 2p orbital. The orbitals having the same energy

are called **degenerate.** The 1s orbital in a hydrogen atom, as said earlier, corresponds to the most stable condition and is called the **ground state** and an electron residing in this orbital is most strongly held by the nucleus. An electron in the 2s, 2p or higher orbitals in a hydrogen atom is in **excited state.**

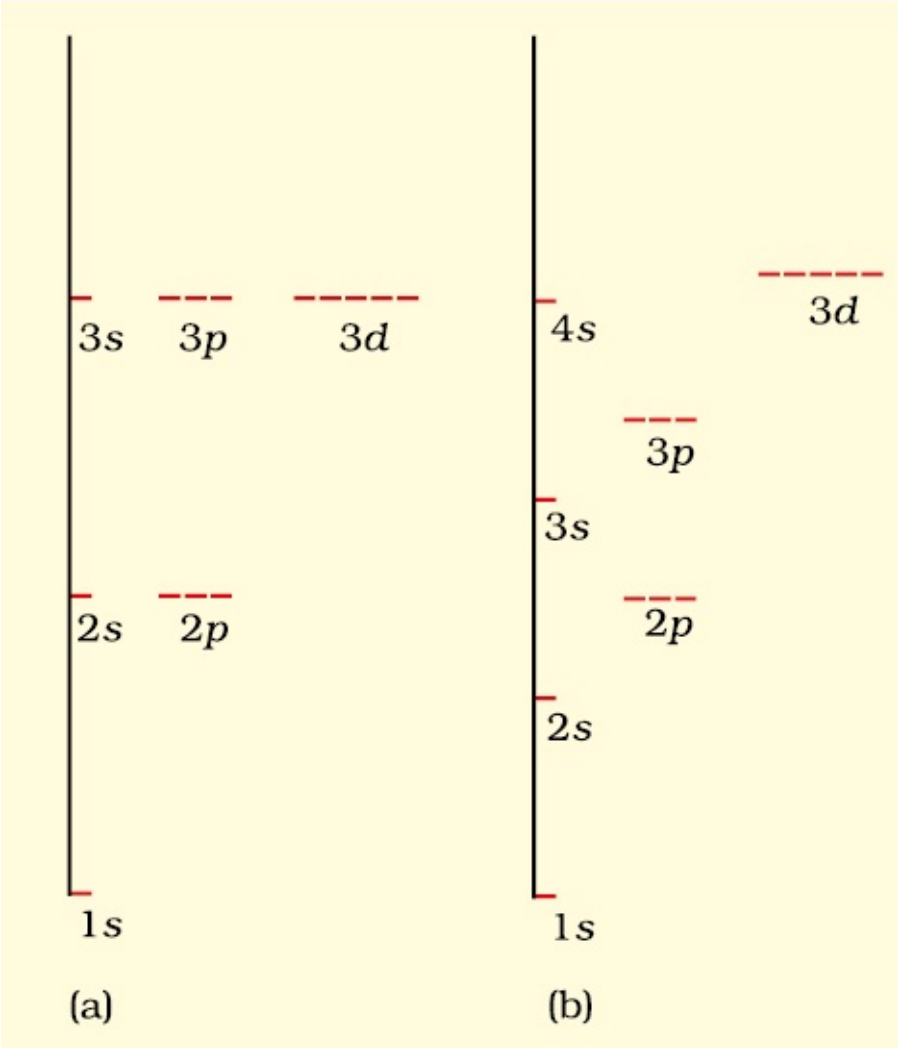


Fig. 2.16 Energy level diagrams for the few electronic shells of (a) hydrogen atom and (b) multi-electronic atoms. Note that orbitals for the same value of principal quantum number, have the same energies even for different azimuthal quantum number for hydrogen atom. In case of multi-electron atoms, orbitals with same principal quantum number possess different energies for different azimuthal quantum numbers.

The energy of an electron in a multi-electron atom, unlike that of the hydrogen atom, depends not only on its principal quantum number (shell), but also on its azimuthal quantum number (subshell). That is, for a given principal quantum number, s, p, d, f ... all have different energies. Within a given principal quantum number, the energy of orbitals increases in the order s<p<d<f. For higher energy levels, these differences are sufficiently pronounced and straggering of orbital energy may result, e.g., 4s<3d and 6s<5d 4f<6p. The main reason for having different energies of the subshells is the mutual repulsion among the electrons in multi-electron atoms. The only electrical interaction present in hydrogen atom is the attraction between the negatively charged electron and the positively charged nucleus. In multi-electron atoms, besides the presence of attraction between the electron and nucleus, there are repulsion terms between every electron and other electrons present in the atom. Thus the stability of an electron in a multi-electron atom is because total attractive interactions are more than the repulsive interactions. In general, the repulsive interaction of the electrons in the outer shell with the electrons in the inner shell are more important. On the other hand, the attractive interactions of an electron increases with increase of positive charge (Ze) on the nucleus. Due to the presence of electrons in the inner shells, the electron in the outer shell will not experience the full positive charge of the nucleus (Ze). The effect will be lowered due to the partial screening of positive charge on the nucleus by the inner shell electrons. This is known as the **shielding of the outer shell electrons from the nucleus by the inner shell electrons,** and the net positive charge experienced by the outer electrons is known as **effective nuclear charge** (Z_{eff} e). Despite the shielding of the outer electrons from the nucleus by the inner shell electrons, the attractive force experienced by the outer shell electrons increases with increase of nuclear charge. In other words, the energy of

interaction between, the nucleus and electron (that is orbital energy) decreases (that is more negative) with the increase of atomic number (Z). Both the attractive and repulsive interactions depend upon the shell and shape of the orbital in which the electron is present. For example electrons present in spherical shaped, s orbital shields the outer electrons from the nucleus more effectively as compared to electrons present in p orbital. Similarly electrons present in p orbitals shield the outer electrons from the nucleus more than the electrons present in d orbitals, even though all these orbitals are present in the same shell. Further within a shell, due to spherical shape of s orbital, the s orbital electron spends more time close to the nucleus in comparison to p orbital electron which spends more time in the vicinity of nucleus in comparison to d orbital electron. In other words, for a given shell (principal quantum number), the Z_{eff} experienced by the electron decreases with increase of azimuthal quantum number (l), that is, the s orbital electron will be more tightly bound to the nucleus than p orbital electron which in turn will be better tightly bound than the d orbital electron. The energy of electrons in s orbital will be lower (more negative) than that of p orbital electron which will have less energy than that of d orbital electron and so on. Since the extent of shielding from the nucleus is different for electrons in different orbitals, it leads to the splitting of energy levels within the same shell (or same principal quantum number), that is, energy of electron in an orbital, as mentioned earlier, depends upon the values of n and l. Mathematically, the dependence of energies of the orbitals on n and l are quite complicated but one simple rule is that, **the lower the value of (**n **+** l**) for an orbital, the lower is its energy. If two orbitals have the same value of (**n **+** l**), the orbital with lower value of** n **will have the lower energy.** The Table 2.5 illustrates the (n + l) rule and Fig. 2.16 depicts the energy levels of multi-electrons atoms. It may be noted that different

subshells of a particular shell have different energies in case of multi–electrons atoms. However, in hydrogen atom, these have the same energy. Lastly it may be mentioned here that **energies of the orbitals in the same subshell decrease with increase in the atomic number (**Z_{eff}**)**. For example, energy of 2s orbital of hydrogen atom is greater than that of 2s orbital of lithium and that of lithium is greater than that of sodium and so on, that is, $E_{2s}(H) > E_{2s}(Li) > E_{2s}(Na) > E_{2s}(K)$.

Table 2.5 Arrangement of Orbitals with Increasing Energy on the Basis of (n+l) Rule

Orbital	Value of n	Value of l	Value of $(n + l)$	
1s	1	0	1 + 0 = 1	
2s	2	0	2 + 0 = 2	
2p	2	1	2 + 1 = 3	2*p* (*n*=2) has lower energy than
3s	3	0	3 + 0 = 3	3*s* (*n*=3)
3p	3	1	3 + 1 = 4	3*p* (*n* =3) has lower energy than
4s	4	0	4 + 0 = 4	4*s* (*n* =4)
3d	3	2	3 + 2 = 5	3*d* (*n* =3) has lower energy than
4p	4	1	4 + 1 =5	4*p* (*n* =4)

2.6.4 Filling of Orbitals in Atom

The filling of electrons into the orbitals of different atoms takes place according to the aufbau principle which is based on the Pauli's exclusion principle, the Hund's rule of maximum multiplicity and the relative energies of the orbitals.

Aufbau Principle

The word ‘aufbau’ in German means ‘building up’. The building up of orbitals means the filling up of orbitals with electrons. The principle states : **In the ground state of the atoms, the orbitals are filled in order of their increasing energies.** In other words, electrons first occupy the lowest energy orbital available to them and enter into higher energy orbitals only after the lower energy orbitals are filled. As you have learnt above, energy of a given orbital depends upon effective nuclear charge and different type of orbitals are affected to different extent. Thus, there is no single ordering of energies of orbitals which will be universally correct for all atoms.

However, following order of energies of the orbitals is extremely useful:

1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 4f, 5d, 6p, 7s...

The order may be remembered by using the method given in Fig. 2.17. Starting from the top, the direction of the arrows gives the order of filling of orbitals, that is starting from right top to bottom left. With respect to placement of outermost valence electrons, it is remarkably accurate for all atoms. for example, valence electron in potassium must choose between 3d and 4s orbitals and as predicted by this sequence, it is found in 4s orbital. The above order should be assumed to be a rough guide to the filling of energy levels. In many cases, the orbitals are similar in energy and small changes in atomic structure may bring about a change in the order of filling. Even then, the above series is a useful guide to the building of the electronic structure of an atom provided that it is remembered that exceptions may occur.

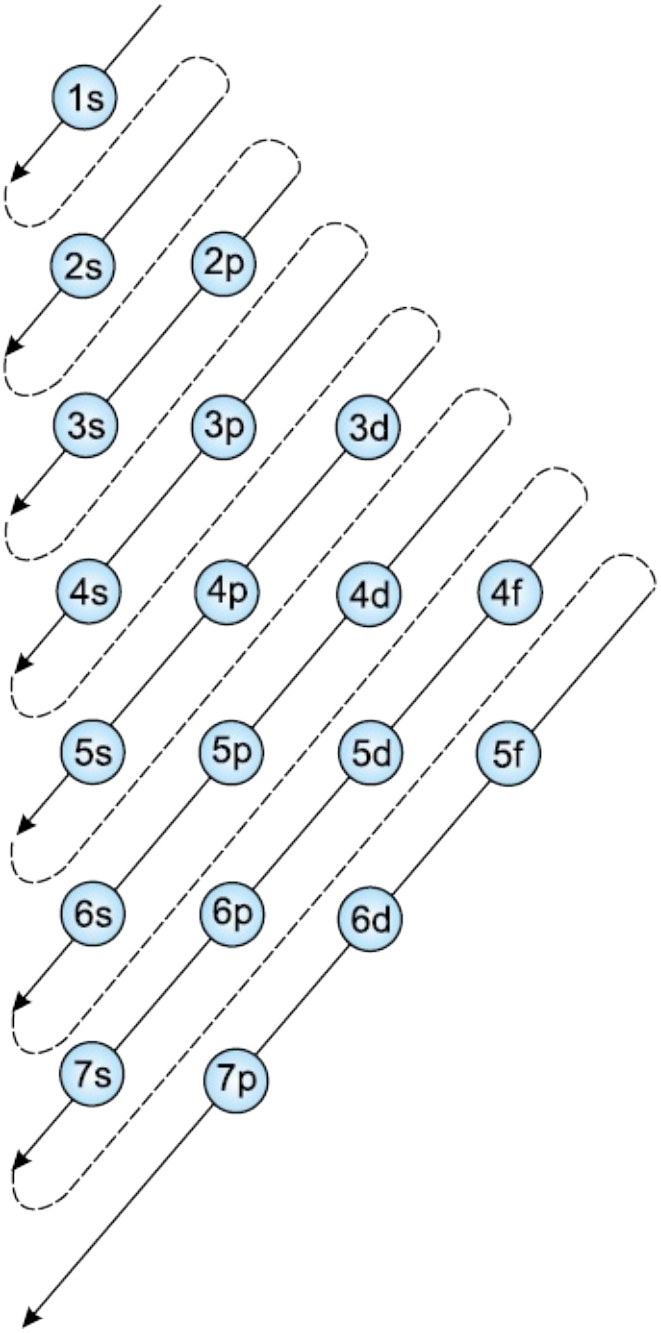


Fig.2.17 Order of filling of orbitals

Pauli Exclusion Principle

The number of electrons to be filled in various orbitals is restricted by the exclusion principle, given by the Austrian scientist Wolfgang Pauli (1926). According to this principle : **No two electrons in an atom can have the**

same set of four quantum numbers. Pauli exclusion principle can also be stated as : **"Only two electrons may exist in the same orbital and these electrons must have opposite spin."** This means that the two electrons can have the same value of three quantum numbers n, l and ml, but must have the opposite spin quantum number. The restriction imposed by Pauli's exclusion principle on the number of electrons in an orbital helps in calculating the capacity of electrons to be present in any subshell. For example, subshell 1s comprises one orbital and thus the maximum number of electrons present in 1s subshell can be two, in p and d subshells, the maximum number of electrons can be 6 and 10 and so on. This can be summed up as : **the maximum number of electrons in the shell with principal quantum number** n **is equal to 2**n^2**.**

Hund's Rule of Maximum Multiplicity

This rule deals with the filling of electrons into the orbitals belonging to the same subshell (that is, orbitals of equal energy, called **degenerate orbitals).** It states : **pairing of electrons in the orbitals belonging to the same subshell (**p**,** d **or** f**) does not take place until each orbital belonging to that subshell has got one electron each i.e., it is singly occupied.**

Since there are three p, five d and seven f orbitals, therefore, the pairing of electrons will start in the p, d and f orbitals with the entry of 4th, 6th and 8th electron, respectively. It has been observed that half filled and fully filled degenerate set of orbitals acquire extra stability due to their symmetry (see Section, 2.6.7).

2.6.5 Electronic Configuration of Atoms

The distribution of electrons into orbitals of an atom is called its **electronic configuration**. If one keeps in mind the basic rules which govern the filling of different atomic orbitals, the electronic configurations of different atoms can be written very easily.

The electronic configuration of different atoms can be represented in two ways. For
example :

(i) $s^a p^b d^c$ ..... notation

(ii) Orbital diagram



In the first notation, the subshell is represented by the respective letter symbol and the number of electrons present in the subshell is depicted, as the super script, like a, b, c, ... etc. The similar subshell represented for different shells is differentiated by writing the principal quantum number before the respective subshell. In the second notation each orbital of the subshell is represented by a box and the electron is represented by an arrow (↑) a positive spin or an arrow (↓) a negative spin. The advantage of second notation over the first is that it represents all the four quantum numbers.

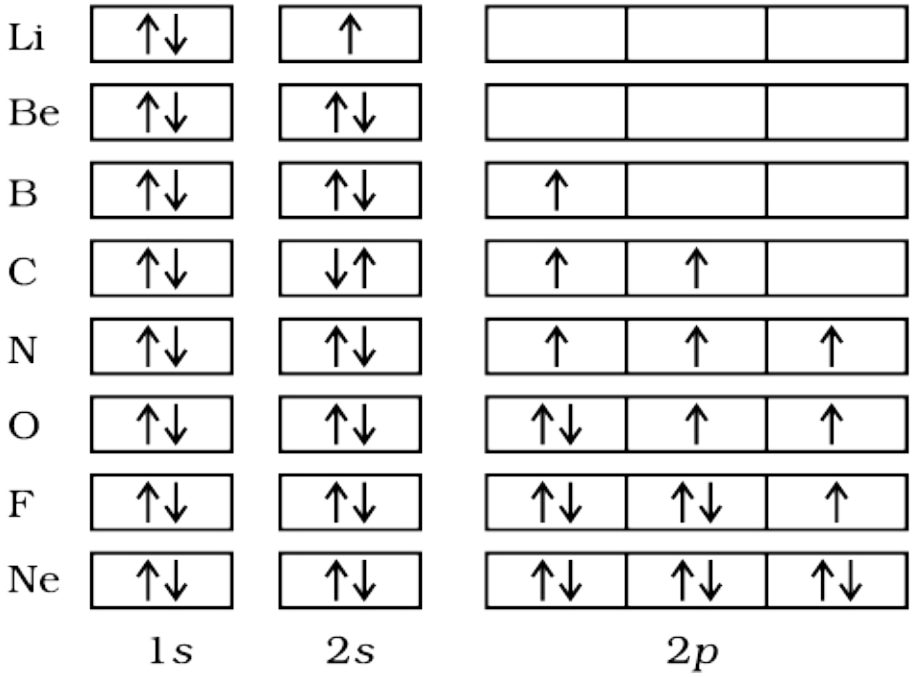
The hydrogen atom has only one electron which goes in the orbital with the lowest energy, namely 1s. The electronic configuration of the hydrogen atom is $1s^1$ meaning that it has one electron in the 1s orbital. The second electron in helium (He) can also occupy the 1s orbital. Its configuration is, therefore, $1s^2$. As mentioned above, the two electrons differ from each other with opposite spin, as can be seen from the orbital diagram.



The third electron of lithium (Li) is not allowed in the 1s orbital because of Pauli exclusion principle. It, therefore, takes the next available choice, namely the 2s orbital. The electronic configuration of Li is $1s^2 2s^1$. The 2s orbital can accommodate one more electron. The configuration of

beryllium (Be) atom is, therefore, $1s^2\ 2s^2$ (see Table 2.6, page 66 for the electronic configurations of elements).

In the next six elements—boron (B, $1s^2 2s^2 2p^1$), carbon (C, $1s^2 2s^2 2p^2$), nitrogen (N, $1s^2 2s^2 2p^3$), oxygen (O, $1s^2 2s^2 2p^4$), fluorine (F, $1s^2 2s^2 2p^5$) and neon (Ne, $1s^2 2s^2 2p^6$), the 2p orbitals get progressively filled. This process is completed with the neon atom. The orbital picture of these elements can be represented as follows :



The electronic configuration of the elements sodium (Na,$1s^2 2s^2 2p^6 3s^1$) to argon (Ar,$1s^2 2s^2 2p^6 3s^2 3p^6$), follow exactly the same pattern as the elements from lithium to neon with the difference that the 3s and 3p orbitals are getting filled now. This process can be simplified if we represent the total number of electrons in the first two shells by the name of element neon (Ne). The electronic configuration of the elements from sodium to argon can be written as (Na, [Ne]$3s^1$) to (Ar, [Ne] $3s^2 3p^6$). The electrons in the completely filled shells are known as core electrons and the electrons that are added to the electronic shell with the highest principal quantum number are called **valence electrons.** For example,

the electrons in Ne are the core electrons and the electrons from Na to Ar are the valence electrons. In potassium (K) and calcium (Ca), the 4s orbital, being lower in energy than the 3d orbitals, is occupied by one and two electrons respectively.

A new pattern is followed beginning with scandium (Sc). The 3d orbital, being lower in energy than the 4p orbital, is filled first. Consequently, in the next ten elements, scandium (Sc), titanium (Ti), vanadium (V), chromium (Cr), manganese (Mn), iron (Fe), cobalt (Co), nickel (Ni), copper (Cu) and zinc (Zn), the five 3d orbitals are progressively occupied. We may be puzzled by the fact that chromium and copper have five and ten electrons in 3d orbitals rather than four and nine as their position would have indicated with two-electrons in the 4s orbital. The reason is that fully filled orbitals and half-filled orbitals have extra stability (that is, lower energy). Thus p^3, p^6, d^5, d^{10},f^{7}, f^{14} etc. configurations, which are either half-filled or fully filled, are more stable. Chromium and copper therefore adopt the d^5 and d^{10} configuration (Section 2.6.7)[caution: exceptions do exist]

With the saturation of the 3d orbitals, the filling of the 4p orbital starts at gallium (Ga) and is complete at krypton (Kr). In the next eighteen elements from rubidium (Rb) to xenon (Xe), the pattern of filling the 5s, 4d and 5p orbitals are similar to that of 4s, 3d and 4p orbitals as discussed above. Then comes the turn of the 6s orbital. In caesium (Cs) and the barium (Ba), this orbital contains one and two electrons, respectively. Then from lanthanum (La) to mercury (Hg), the filling up of electrons takes place in 4f and 5d orbitals. After this, filling of 6p, then 7s and finally 5f and 6d orbitals takes place. The elements after uranium (U) are all short-lived and all of them are produced artificially. The electronic configurations of the known elements (as determined by spectroscopic

methods) are tabulated in Table 2.6 (page 66).

One may ask what is the utility of knowing the electron configuration? The modern approach to the chemistry, infact, depends almost entirely on electronic distribution to understand and explain chemical behaviour. For example, questions like why two or more atoms combine to form molecules, why some elements are metals while others are non-metals, why elements like helium and argon are not reactive but elements like the halogens are reactive, find simple explanation from the electronic configuration. These questions have no answer in the Daltonian model of atom. A detailed understanding of the electronic structure of atom is, therefore, very essential for getting an insight into the various aspects of modern chemical knowledge.

2.6.6 Stability of Completely Filled and Half Filled Subshells

The ground state electronic configuration of the atom of an element always corresponds to the state of the lowest total electronic energy. The electronic configurations of most of the atoms follow the basic rules given in Section 2.6.5. However, in certain elements such as Cu, or Cr, where the two subshells (4s and 3d) differ slightly in their energies, an electron shifts from a subshell of lower energy (4s) to a subshell of higher energy (3d), provided such a shift results in all orbitals of the subshell of higher energy getting either completely filled or half filled. The valence electronic configurations of Cr and Cu, therefore, are 3d5 4s1 and 3d10 4s1 respectively and not 3d4 4s2 and 3d9 4s2. It has been found that there is extra stability associated with these electronic configurations.

Causes of Stability of Completely Filled and Half-filled Subshells

The completely filled and completely

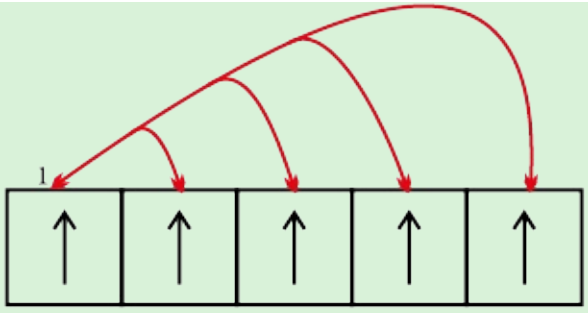
half-filled subshells are stable due to the following reasons:

1.Symmetrical distribution of electrons: It is well known that symmetry leads to stability.

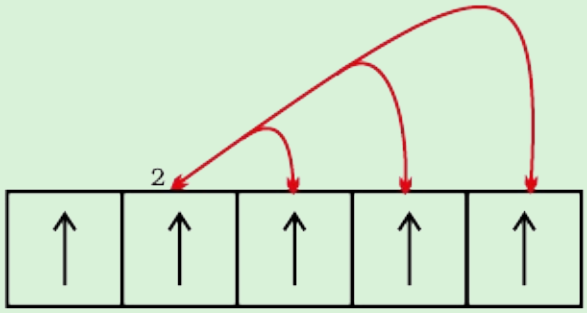
The completely filled or half filled subshells have symmetrical distribution of electrons in them and are therefore more stable. Electrons in the same subshell (here 3d) have equal energy but different spatial distribution. Consequently, their shielding of one-another is relatively small and the electrons are more strongly attracted by the nucleus.

2. Exchange Energy : The stabilizing effect arises whenever two or more electrons with the same spin are present in the degenerate orbitals of a subshell. These electrons tend to exchange their positions and the energy released due to this exchange is called exchange energy. The number of exchanges that can take place is maximum when the subshell is either half filled or completely filled (Fig. 2.18). As a result the exchange energy is maximum and so is the stability.

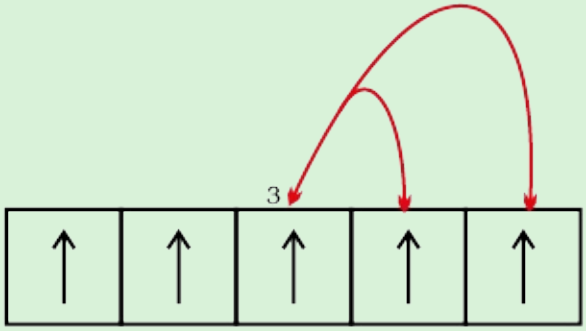
You may note that the exchange energy is at the basis of Hund's rule that electrons which enter orbitals of equal energy have parallel spins as far as possible. In other words, the extra stability of half-filled and completely filled subshell is due to: (i) relatively small shielding, (ii) smaller coulombic repulsion energy, and (iii) larger exchange energy. Details about the exchange energy will be dealt with in higher classes.



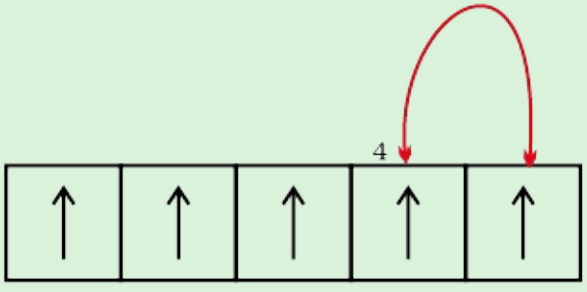
4 exchange by electron 1



3 exchange by electron 2



2 exchange by electron 3



1 exchange by electron 4

Fig. 2.18 Possible exchange for a d5 configuration

Table 2.6 Electronic Configurations of the Elements

Element	Z	1s	2s	2p	3s	3p	3d	4s	4p	4d	4f	5s	5p	5d	5f	6s	6p	6d	7s
H	1	1																	
He	2	2																	
Li	3	2	1																
Be	4	2	2																
B	5	2	2	1															
C	6	2	2	2															
N	7	2	2	3															
O	8	2	2	4															
F	9	2	2	5															
Ne	10	2	2	6															
Na	11	2	2	6	1														
Mg	12	2	2	6	2														
Al	13	2	2	6	2	1													
Si	14	2	2	6	2	2													
P	15	2	2	6	2	3													
S	16	2	2	6	2	4													
Cl	17	2	2	6	2	5													
Ar	18	2	2	6	2	6													
K	19	2	2	6	2	6		1											
Ca	20	2	2	6	2	6		2											
Sc	21	2	2	6	2	6	1	2											
Ti	22	2	2	6	2	6	2	2											
V	23	2	2	6	2	6	3	2											
Cr*	24	2	2	6	2	6	5	1											
Mn	25	2	2	6	2	6	5	2											
Fe	26	2	2	6	2	6	6	2											
Co	27	2	2	6	2	6	7	2											
Ni	28	2	2	6	2	6	8	2											
Cu*	29	2	2	6	2	6	10	1											
Zn	30	2	2	6	2	6	10	2											
Ga	31	2	2	6	2	6	10	2	1										
Ge	32	2	2	6	2	6	10	2	2										
As	33	2	2	6	2	6	10	2	3										
Se	34	2	2	6	2	6	10	2	4										
Br	35	2	2	6	2	6	10	2	5										
Kr	36	2	2	6	2	6	10	2	6										
Rb	37	2	2	6	2	6	10	2	6			1							
Sr	38	2	2	6	2	6	10	2	6			2							
Y	39	2	2	6	2	6	10	2	6	1		2							
Zr	40	2	2	6	2	6	10	2	6	2		2							
Nb*	41	2	2	6	2	6	10	2	6	4		1							
Mo*	42	2	2	6	2	6	10	2	6	5		1							
Tc	43	2	2	6	2	6	10	2	6	5		2							
Ru*	44	2	2	6	2	6	10	2	6	7		1							
Rh*	45	2	2	6	2	6	10	2	6	8		1							
Pd*	46	2	2	6	2	6	10	2	6	10									
Ag*	47	2	2	6	2	6	10	2	6	10		1							
Cd	48	2	2	6	2	6	10	2	6	10		2							
In	49	2	2	6	2	6	10	2	6	10		2	1						
Sn	50	2	2	6	2	6	10	2	6	10		2	2						
Sb	51	2	2	6	2	6	10	2	6	10		2	3						
Te	52	2	2	6	2	6	10	2	6	10		2	4						
I	53	2	2	6	2	6	10	2	6	10		2	5						
Xe	54	2	2	6	2	6	10	2	6	10		2	6						

* Elements with exceptional electronic configurations

Element	Z	1s	2s	2p	3s	3p	3d	4s	4p	4d	4f	5s	5p	5d	5f	6s	6p	6d	7s
Cs	55	2	2	6	2	6	10	2	6	10		2	6			1			
Ba	56	2	2	6	2	6	10	2	6	10		2	6			2			
La*	57	2	2	6	2	6	10	2	6	10		2	6	1		2			
Ce*	58	2	2	6	2	6	10	2	6	10	2	2	6			2			
Pr	59	2	2	6	2	6	10	2	6	10	3	2	6			2			
Nd	60	2	2	6	2	6	10	2	6	10	4	2	6			2			
Pm	61	2	2	6	2	6	10	2	6	10	5	2	6			2			
Sm	62	2	2	6	2	6	10	2	6	10	6	2	6			2			
Eu	63	2	2	6	2	6	10	2	6	10	7	2	6			2			
Gd*	64	2	2	6	2	6	10	2	6	10	7	2	6	1		2			
Tb	65	2	2	6	2	6	10	2	6	10	9	2	6			2			
Dy	66	2	2	6	2	6	10	2	6	10	10	2	6			2			
Ho	67	2	2	6	2	6	10	2	6	10	11	2	6			2			
Er	68	2	2	6	2	6	10	2	6	10	12	2	6			2			
Tm	69	2	2	6	2	6	10	2	6	10	13	2	6			2			
Yb	70	2	2	6	2	6	10	2	6	10	14	2	6			2			
Lu	71	2	2	6	2	6	10	2	6	10	14	2	6	1		2			
Hf	72	2	2	6	2	6	10	2	6	10	14	2	6	2		2			
Ta	73	2	2	6	2	6	10	2	6	10	14	2	6	3		2			
W	74	2	2	6	2	6	10	2	6	10	14	2	6	4		2			
Re	75	2	2	6	2	6	10	2	6	10	14	2	6	5		2			
Os	76	2	2	6	2	6	10	2	6	10	14	2	6	6		2			
Ir	77	2	2	6	2	6	10	2	6	10	14	2	6	7		2			
Pt*	78	2	2	6	2	6	10	2	6	10	14	2	6	9		1			
Au*	79	2	2	6	2	6	10	2	6	10	14	2	6	10		1			
Hg	80	2	2	6	2	6	10	2	6	10	14	2	6	10		2			
Tl	81	2	2	6	2	6	10	2	6	10	14	2	6	10		2	1		
Pb	82	2	2	6	2	6	10	2	6	10	14	2	6	10		2	2		
Bi	83	2	2	6	2	6	10	2	6	10	14	2	6	10		2	3		
Po	84	2	2	6	2	6	10	2	6	10	14	2	6	10		2	4		
At	85	2	2	6	2	6	10	2	6	10	14	2	6	10		2	5		
Rn	86	2	2	6	2	6	10	2	6	10	14	2	6	10		2	6		
Fr	87	2	2	6	2	6	10	2	6	10	14	2	6	10		2	6		1
Ra	88	2	2	6	2	6	10	2	6	10	14	2	6	10		2	6		2
Ac	89	2	2	6	2	6	10	2	6	10	14	2	6	10		2	6	1	2
Th	90	2	2	6	2	6	10	2	6	10	14	2	6	10		2	6	2	2
Pa	91	2	2	6	2	6	10	2	6	10	14	2	6	10	2	2	6	1	2
U	92	2	2	6	2	6	10	2	6	10	14	2	6	10	3	2	6	1	2
Np	93	2	2	6	2	6	10	2	6	10	14	2	6	10	4	2	6	1	2
Pu	94	2	2	6	2	6	10	2	6	10	14	2	6	10	6	2	6		2
Am	95	2	2	6	2	6	10	2	6	10	14	2	6	10	7	2	6		2
Cm	96	2	2	6	2	6	10	2	6	10	14	2	6	10	7	2	6	1	2
Bk	97	2	2	6	2	6	10	2	6	10	14	2	6	10	8	2	6	1	2
Cf	98	2	2	6	2	6	10	2	6	10	14	2	6	10	10	2	6		2
Es	99	2	2	6	2	6	10	2	6	10	14	2	6	10	11	2	6		2
Fm	100	2	2	6	2	6	10	2	6	10	14	2	6	10	12	2	6		2
Md	101	2	2	6	2	6	10	2	6	10	14	2	6	10	13	2	6		2
No	102	2	2	6	2	6	10	2	6	10	14	2	6	10	14	2	6		2
Lr	103	2	2	6	2	6	10	2	6	10	14	2	6	10	14	2	6	1	2
Rf	104	2	2	6	2	6	10	2	6	10	14	2	6	10	10	2	6	2	2
Db	105	2	2	6	2	6	10	2	6	10	14	2	6	10	11	2	6	3	2
Sg	106	2	2	6	2	6	10	2	6	10	14	2	6	10	12	2	6	4	2
Bh	107	2	2	6	2	6	10	2	6	10	14	2	6	10	13	2	6	5	2
Hs	108	2	2	6	2	6	10	2	6	10	14	2	6	10	14	2	6	6	2
Mt	109	2	2	6	2	6	10	2	6	10	14	2	6	10	14	2	6	7	2
Ds	110	2	2	6	2	6	10	2	6	10	14	2	6	10	14	2	6	8	2
Rg**	111	2	2	6	2	6	10	2	6	10	14	2	6	10	14	2	6	10	1

** Elements with atomic number 112 and above have been reported but not yet fully authenticated and named.

Summary

Atoms are the building blocks of elements. They are the smallest parts of an element that chemically react. The first atomic theory, proposed by John Dalton in 1808, regarded atom as the ultimate indivisible particle of matter. Towards the end of the nineteenth century, it was proved experimentally that atoms are divisible and consist of three fundamental particles: **electrons**, **protons** and **neutrons**. The discovery of sub-atomic particles led to the proposal of various atomic models to explain the structure of atom.

Thomson in 1898 proposed that an atom consists of uniform sphere of positive electricity with electrons embedded into it. This model in which mass of the atom is considered to be evenly spread over the atom was proved wrong by Rutherford's famous alpha-particle scattering experiment in 1909. Rutherford concluded that atom is made of a tiny positively charged **nucleus**, at its centre with electrons revolving around it in **circular orbits**. **Rutherford model**, which resembles the solar system, was no doubt an improvement over **Thomson model** but it could not account for the stability of the atom i.e., why the electron does not fall into the nucleus. Further, it was also silent about the electronic structure of atoms i.e., about the distribution and relative energies of electrons around the nucleus. The difficulties of the Rutherford model were overcome by Niels Bohr in 1913 in his model of the hydrogen atom. Bohr postulated that electron moves around the nucleus in circular orbits. Only certain orbits can exist and each orbit corresponds to a specific energy. Bohr calculated the energy of electron in various orbits and for each orbit predicted the distance between the electron and nucleus. **Bohr model**, though offering a satisfactory model for explaining the spectra of the hydrogen atom, could not explain the spectra of multi-electron atoms. The reason for this was soon discovered. In Bohr model, an electron is regarded as a charged particle moving in a well defined circular orbit about the nucleus. The wave character of the electron is ignored in Bohr's theory. An orbit is a clearly defined path and this path can completely be defined only if both the exact position and the exact velocity of the electron at the same time are known. This is not possible according to the Heisenberg uncertainty principle. Bohr model of the hydrogen atom, therefore, not only ignores the dual behaviour of electron but also contradicts **Heisenberg uncertainty principle**.

Erwin Schrödinger, in 1926, proposed an equation called Schrödinger equation to describe the electron distributions in space and the allowed energy levels in atoms. This equation incorporates de Broglie's concept of **wave-particle duality** and is consistent with Heisenberg uncertainty principle. When Schrödinger equation is solved for the electron in a hydrogen atom, the solution gives the possible energy states the electron can occupy [and the corresponding wave function(s) (ψ) (which in fact are the mathematical functions) of the electron associated with each energy state]. These quantized energy states and corresponding wave functions which are characterized by a set of three quantum numbers (**principal quantum number** n, **azimuthal quantum number** l and **magnetic quantum number** ml) arise as a natural consequence in the solution of the Schrödinger equation. The restrictions on the values of these three quantum numbers also come naturally from this solution. The quantum mechanical model of the hydrogen atom successfully predicts all aspects of the hydrogen atom spectrum including some phenomena that could not be explained by the Bohr model.

According to the quantum mechanical model of the atom, the electron distribution of an atom containing a number of electrons is divided into **shells**. The shells, in turn, are thought to consist of one or more **subshells** and subshells are assumed to be composed of one or more orbitals, which the electrons occupy. While for hydrogen and hydrogen like systems (such as He^{+}, Li^{2+} etc.) all the orbitals within a given shell have same energy, the energy of the orbitals in a multi-electron atom depends upon the values of n and l: The lower the value of (n + l) for an orbital, the lower is its energy. If two orbitals have the same (n + l) value, the orbital with lower value of n has the lower energy. In an atom many such orbitals are possible and electrons are filled in those orbitals in order of increasing energy in accordance with **Pauli exclusion principle** (no two electrons in an atom can have the same set of four quantum numbers) and **Hund's rule of maximum multiplicity** (pairing of electrons in the orbitals belonging to the same subshell does not take place until each orbital belonging to that subshell has got one electron each, i.e., is singly occupied). This forms the basis of the electronic structure of atoms.

EXERCISES

2.1 (i) Calculate the number of electrons which will together weigh one

gram.

(ii) Calculate the mass and charge of one mole of electrons.

2.2 (i) Calculate the total number of electrons present in one mole of methane.

(ii) Find (a) the total number and (b) the total mass of neutrons in 7 mg of ^{14}C. (Assume that mass of a neutron = 1.675×10^{-27} kg).

(iii) Find (a) the total number and (b) the total mass of protons in 34 mg of NH3 at STP.

Will the answer change if the temperature and pressure are changed ?

2.3 How many neutrons and protons are there in the following nuclei ?

$^{13}_{6}C$, $^{16}_{8}O$, $^{24}_{12}Mg$, $^{56}_{26}Fe$, $^{88}_{38}Sr$

2.4 Write the complete symbol for the atom with the given atomic number (Z) and atomic mass (A)

(i) Z = 17 , A = 35.

(ii) Z = 92 , A = 233.

(iii) Z = 4 , A = 9.

2.5 Yellow light emitted from a sodium lamp has a wavelength (λ) of 580 nm. Calculate the frequency (v) and wavenumber ($\overline{\nu}$) of the yellow light.

2.6 Find energy of each of the photons which

(i) correspond to light of frequency 3×10^{15} Hz.

(ii) have wavelength of 0.50 Å.

2.7 Calculate the wavelength, frequency and wavenumber of a light wave whose period is 2.0×10^{-10} s.

2.8 What is the number of photons of light with a wavelength of 4000 pm that provide 1J of energy?

2.9 A photon of wavelength 4×10^{-7} m strikes on metal surface, the work function of the metal being 2.13 eV. Calculate (i) the energy of the photon (eV), (ii) the kinetic energy of the emission, and (iii) the velocity of the photoelectron

(1 eV= 1.6020×10^{-19} J).

2.10 Electromagnetic radiation of wavelength 242 nm is just sufficient to ionise the sodium atom. Calculate the ionisation energy of sodium in kJ mol^{-1}.

2.11 A 25 watt bulb emits monochromatic yellow light of wavelength of 0.57μm. Calculate the rate of emission of quanta per second.

2.12 Electrons are emitted with zero velocity from a metal surface when it is exposed to radiation of wavelength 6800 Å. Calculate threshold frequency (v0) and work function (W0) of the metal.

2.13 What is the wavelength of light emitted when the electron in a hydrogen atom undergoes transition from an energy level with n = 4 to an energy level with n = 2?

2.14 How much energy is required to ionise a H atom if the electron occupies n = 5 orbit? Compare your answer with the ionization enthalpy of H atom (energy required to remove the electron from n =1 orbit).

2.15 What is the maximum number of emission lines when the excited electron of a H atom in n = 6 drops to the ground state?

2.16 (i) The energy associated with the first orbit in the hydrogen atom is -2.18×10^{-18} J $atom^{-1}$. What is the energy associated with the fifth orbit? (ii) Calculate the radius of Bohr's fifth orbit for hydrogen atom.

2.17 Calculate the wavenumber for the longest wavelength transition in the Balmer series of atomic hydrogen.

2.18 What is the energy in joules, required to shift the electron of the hydrogen atom from the first Bohr orbit to the fifth Bohr orbit and what is the wavelength of the light emitted when the electron returns to the ground state? The ground state electron energy is -2.18×10^{-11} ergs.

2.19 The electron energy in hydrogen atom is given by $E_n = (-2.18 \times 10^{-18})/n^2$ J. Calculate the energy required to remove an electron completely from the n = 2 orbit. What is the longest wavelength of light in cm that

can be used to cause this transition?

2.20 Calculate the wavelength of an electron moving with a velocity of 2.05×10^7 m s^{-1}.

2.21 The mass of an electron is 9.1×10^{-31} kg. If its K.E. is 3.0×10^{-25} J, calculate its wavelength.

2.22 Which of the following are isoelectronic species i.e., those having the same number of electrons?

Na^+, K^+, Mg^{2+}, Ca^{2+}, S^{2-}, Ar.

2.23 (i) Write the electronic configurations of the following ions: (a) H^- (b) Na^+ (c) O^{2-}

(d) F^-

(ii) What are the atomic numbers of elements whose outermost electrons are represented by (a) $3s^1$ (b) $2p^3$ and (c) $3p^5$?

(iii) Which atoms are indicated by the following configurations ?

(a) [He] $2s^1$ (b) [Ne] $3s^2$ $3p^3$ (c) [Ar] $4s^2$ $3d^1$.

2.24 What is the lowest value of n that allows g orbitals to exist?

2.25 An electron is in one of the 3d orbitals. Give the possible values of n, l and ml for this electron.

2.26 An atom of an element contains 29 electrons and 35 neutrons. Deduce (i) the number of protons and (ii) the electronic configuration of the element.

2.27 Give the number of electrons in the species H_2^+, H_2 and O_2^+

2.28 (i) An atomic orbital has n = 3. What are the possible values of l and ml ?

(ii) List the quantum numbers (ml and l) of electrons for 3d orbital.

(iii) Which of the following orbitals are possible?

1p, 2s, 2p and 3f

2.29 Using s, p, d notations, describe the orbital with the following

quantum numbers.

(a) n=1, l=0; (b) n = 3; l=1 (c) n = 4; l =2; (d) n=4; l=3.

2.30 Explain, giving reasons, which of the following sets of quantum numbers are not possible.

(a) n = 0, l = 0, ml = 0, ms = + ½

(b) n = 1, l = 0, ml = 0, ms = – ½

(c) n = 1, l = 1, ml = 0, ms = + ½

(d) n = 2, l = 1, ml = 0, ms = – ½

(e) n = 3, l = 3, ml = –3, ms = + ½

(f) n = 3, l = 1, ml = 0, ms = + ½

2.31 How many electrons in an atom may have the following quantum numbers?

(a) n = 4, ms = – ½ (b) n = 3, l = 0

2.32 Show that the circumference of the Bohr orbit for the hydrogen atom is an integral multiple of the de Broglie wavelength associated with the electron revolving around the orbit.

2.33 What transition in the hydrogen spectrum would have the same wavelength as the Balmer transition n = 4 to n = 2 of He^+ spectrum ?

2.34 Calculate the energy required for the process

$He^+ (g) \blacksquare He^{2+} (g) + e^-$

The ionization energy for the H atom in the ground state is 2.18×10^{-18} J $atom^{-1}$

2.35 If the diameter of a carbon atom is 0.15 nm, calculate the number of carbon atoms which can be placed side by side in a straight line across length of scale of length 20 cm long.

2.36 2×10^8 atoms of carbon are arranged side by side. Calculate the radius of carbon atom if the length of this arrangement is 2.4 cm.

2.37 The diameter of zinc atom is 2.6 Å.Calculate (a) radius of zinc atom in pm and (b) number of atoms present in a length of 1.6 cm if the zinc

atoms are arranged side by side lengthwise.

2.38 A certain particle carries 2.5×10^{-16}C of static electric charge. Calculate the number of electrons present in it.

2.39 In Milikan's experiment, static electric charge on the oil drops has been obtained by shining X-rays. If the static electric charge on the oil drop is -1.282×10^{-18}C, calculate the number of electrons present on it.

2.40 In Rutherford's experiment, generally the thin foil of heavy atoms, like gold, platinum etc. have been used to be bombarded by the α-particles. If the thin foil of light atoms like aluminium etc. is used, what difference would be observed from the above results ?

2.41 Symbols $^{79}_{35}\mathrm{Br}$ and ^{79}Br can be written, whereas symbols $^{35}_{79}\mathrm{Br}$ and ^{35}Br are not acceptable. Answer briefly.

2.42 An element with mass number 81 contains 31.7% more neutrons as compared to protons. Assign the atomic symbol.

2.43 An ion with mass number 37 possesses one unit of negative charge. If the ion conatins 11.1% more neutrons than the electrons, find the symbol of the ion.

2.44 An ion with mass number 56 contains 3 units of positive charge and 30.4% more neutrons than electrons. Assign the symbol to this ion.

2.45 Arrange the following type of radiations in increasing order of frequency: (a) radiation from microwave oven (b) amber light from traffic signal (c) radiation from FM radio (d) cosmic rays from outer space and (e) X-rays.

2.46 Nitrogen laser produces a radiation at a wavelength of 337.1 nm. If the number of photons emitted is 5.6×10^{24}, calculate the power of this laser.

2.47 Neon gas is generally used in the sign boards. If it emits strongly at 616 nm, calculate (a) the frequency of emission, (b) distance traveled by

this radiation in

30 s (c) energy of quantum and (d) number of quanta present if it produces 2 J of energy.

2.48 In astronomical observations, signals observed from the distant stars are generally weak. If the photon detector receives a total of 3.15×10^{-18} J from the radiations of 600 nm, calculate the number of photons received by the detector.

2.49 Lifetimes of the molecules in the excited states are often measured by using pulsed radiation source of duration nearly in the nano second range. If the radiation source has the duration of 2 ns and the number of photons emitted during the pulse source is 2.5×10^{15}, calculate the energy of the source.

2.50 The longest wavelength doublet absorption transition is observed at 589 and 589.6 nm. Calcualte the frequency of each transition and energy difference between two excited states.

2.51 The work function for caesium atom is 1.9 eV. Calculate (a) the threshold wavelength and (b) the threshold frequency of the radiation. If the caesium element is irradiated with a wavelength 500 nm, calculate the kinetic energy and the velocity of the ejected photoelectron.

2.52 Following results are observed when sodium metal is irradiated with different wavelengths. Calculate (a) threshold wavelength and, (b) Planck's constant.

λ (nm)	500	450	400
$v \times 10^{-5}$ (cm s^{-1})	2.55	4.35	5.35

2.53 The ejection of the photoelectron from the silver metal in the photoelectric effect experiment can be stopped by applying the voltage of 0.35 V when the radiation 256.7 nm is used. Calculate the work function for silver metal.

2.54 If the photon of the wavelength 150 pm strikes an atom and one of

tis inner bound electrons is ejected out with a velocity of 1.5×10^7 m s^{-1}, calculate the energy with which it is bound to the nucleus.

2.55 Emission transitions in the Paschen series end at orbit n = 3 and start from orbit n and can be represeted as $v = 3.29 \times 10^{15}$ (Hz) [$1/3^2 - 1/n^2$]

Calculate the value of n if the transition is observed at 1285 nm. Find the region of the spectrum.

2.56 Calculate the wavelength for the emission transition if it starts from the orbit having radius 1.3225 nm and ends at 211.6 pm. Name the series to which this transition belongs and the region of the spectrum.

2.57 Dual behaviour of matter proposed by de Broglie led to the discovery of electron microscope often used for the highly magnified images of biological molecules and other type of material. If the velocity of the electron in this microscope is 1.6×10^6 ms^{-1}, calculate de Broglie wavelength associated with this electron.

2.58 Similar to electron diffraction, neutron diffraction microscope is also used for the determination of the structure of molecules. If the wavelength used here is 800 pm, calculate the characteristic velocity associated with the neutron.

2.59 If the velocity of the electron in Bohr's first orbit is 2.19×10^6 ms^{-1}, calculate the

de Broglie wavelength associated with it.

2.60 The velocity associated with a proton moving in a potential difference of 1000 V is 4.37×10^5 ms^{-1}. If the hockey ball of mass 0.1 kg is moving with this velocity, calcualte the wavelength associated with this velocity.

2.61 If the position of the electron is measured within an accuracy of + 0.002 nm, calculate the uncertainty in the momentum of the electron. Suppose the momentum of the electron is $h/4\pi m \times 0.05$ nm, is there any

problem in defining this value.

2.62 The quantum numbers of six electrons are given below. Arrange them in order of increasing energies. If any of these combination(s) has/have the same energy lists:

1. n = 4, l = 2, ml = –2 , ms = –1/2
2. n = 3, l = 2, ml = 1 , ms = +1/2
3. n = 4, l = 1, ml = 0 , ms = +1/2
4. n = 3, l = 2, ml = –2 , ms = –1/2
5. n = 3, l = 1, ml = –1 , ms = +1/2
6. n = 4, l = 1, ml = 0 , ms = +1/2

2.63 The bromine atom possesses 35 electrons. It contains 6 electrons in 2p orbital, 6 electrons in 3p orbital and 5 electron in 4p orbital. Which of these electron experiences the lowest effective nuclear charge ?

2.64 Among the following pairs of orbitals which orbital will experience the larger effective nuclear charge? (i) 2s and 3s, (ii) 4d and 4f, (iii) 3d and 3p.

2.65 The unpaired electrons in Al and Si are present in 3p orbital. Which electrons will experience more effective nuclear charge from the nucleus ?

2.66 Indicate the number of unpaired electrons in : (a) P, (b) Si, (c) Cr, (d) Fe and (e) Kr.

2.67 (a) How many subshells are associated with n = 4 ? (b) How many electrons will be present in the subshells having ms value of –1/2 for n = 4 ?

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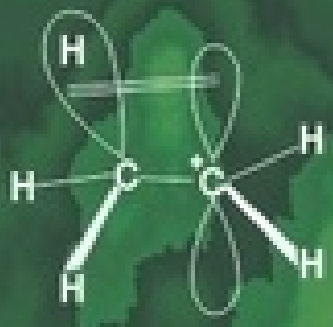
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Textbook for Class XI

Unit 3
Classification of Elements and Periodicity in Properties

Chemistry

Part I



11082CH03

Unit 3

Classification of Elements and Periodicity in Properties

After studying this Unit, you will be able to

- appreciate how the concept of grouping elements in accordance to their properties led to the development of Periodic Table.
- understand the Periodic Law;
- understand the significance of atomic number and electronic configuration as the basis for periodic classification;
- name the elements with Z >100 according to IUPAC nomenclature;
- classify elements into s, p, d, f blocks and learn their main characteristics;
- recognise the periodic trends in physical and chemical properties of elements;
- compare the reactivity of elements and correlate it with their occurrence in nature;
- explain the relationship between ionization enthalpy and metallic character;
- use scientific vocabulary appropriately to communicate ideas related to certain important properties of atoms e.g., atomic/ ionic radii, ionization enthalpy, electron gain enthalpy, electronegativity, valence of elements.

The Periodic Table is arguably the most important concept in

chemistry, both in principle and in practice. It is the everyday support for students, it suggests new avenues of research to professionals, and it provides a succinct organization of the whole of chemistry. It is a remarkable demonstration of the fact that the chemical elements are not a random cluster of entities but instead display trends and lie together in families. An awareness of the Periodic Table is essential to anyone who wishes to disentangle the world and see how it is built up from the fundamental building blocks of the chemistry, the chemical elements.

Glenn T. Seaborg

In this Unit, we will study the historical development of the Periodic Table as it stands today and the Modern Periodic Law. We will also learn how the periodic classification follows as a logical consequence of the electronic configuration of atoms. Finally, we shall examine some of the periodic trends in the physical and chemical properties of the elements.

3.1 WHY DO WE NEED TO CLASSIFY ELEMENTS ?

We know by now that the elements are the basic units of all types of matter. In 1800, only 31 elements were known. By 1865, the number of identified elements had more than doubled to 63. At present 114 elements are known. Of them, the recently discovered elements are man-made. Efforts to synthesise new elements are continuing. With such a large number of elements it is very difficult to study individually the chemistry of all these elements and their innumerable compounds individually. To ease out this problem, scientists searched for a systematic way to organise their knowledge by classifying the elements. Not only that it would rationalize known chemical facts about elements, but even predict new ones for undertaking further study.

3.2 GENESIS OF PERIODIC CLASSIFICATION

Classification of elements into groups and development of Periodic Law

and Periodic Table are the consequences of systematising the knowledge gained by a number of scientists through their observations and experiments. The German chemist, Johann Dobereiner in early 1800's was the first to consider the idea of trends among properties of elements. By 1829 he noted a similarity among the physical and chemical properties of several groups of three elements (**Triads**). In each case, he noticed that the middle element of each of the **Triads** had an atomic weight about half way between the atomic weights of the other two (Table 3.1). Also the properties of the middle element were in between those of the other two members. Since Dobereiner's relationship, referred to as the **Law of Triads**, seemed to work only for a few elements, it was dismissed as coincidence. The next reported attempt to classify elements was made by a French geologist, A.E.B. de Chancourtois in 1862. He arranged the then known elements in order of increasing atomic weights and made a cylindrical table of elements to display the periodic recurrence of properties. This also did not attract much attention. The English chemist, John Alexander Newlands in 1865 profounded the **Law of Octaves**. He arranged the elements in increasing order of their atomic weights and noted that every eighth element had properties similar to the first element (Table 3.2). The relationship was just like every eighth note that resembles the first in octaves of music. Newlands's Law of Octaves seemed to be true only for elements up to calcium. Although his idea was not widely accepted at that time, he, for his work, was later awarded Davy Medal in 1887 by the Royal Society, London.

Table 3.1 Dobereiner's Triads

Element	Atomic weight	Element	Atomic weight	Element	Atomic weight
Li	7	**Ca**	40	**Cl**	35.5
Na	23	**Sr**	88	**Br**	80
K	39	**Ba**	137	**I**	127

The Periodic Law, as we know it today owes its development to the Russian chemist, Dmitri Mendeleev (1834-1907) and the German chemist, Lothar Meyer (1830-1895). Working independently, both the chemists in 1869 proposed that on arranging elements in the increasing order of their atomic weights, similarities appear in physical and chemical properties at regular intervals. Lothar Meyer plotted the physical properties such as atomic volume, melting point and boiling point against atomic weight and obtained a periodically repeated pattern. Unlike Newlands, Lothar Meyer observed a change in length of that repeating pattern. By 1868, Lothar Meyer had developed a table of the elements that closely resembles the Modern Periodic Table. However, his work was not published until after the work of Dmitri Mendeleev, the scientist who is generally credited with the development of the Modern Periodic Table.

Table 3.2 Newlands' Octaves

Element	**Li**	**Be**	**B**	**C**	**N**	**O**	**F**
At. wt.	7	9	11	12	14	16	19
Element	**Na**	**Mg**	**Al**	**Si**	**P**	**S**	**Cl**
At. wt.	23	24	27	29	31	32	35.5
Element	**K**	**Ca**					
At. wt.	39	40					

While Dobereiner initiated the study of periodic relationship, it was Mendeleev who was responsible for publishing the Periodic Law for the first time. It states as follows :

The properties of the elements are a periodic function of their atomic weights.

Mendeleev arranged elements in horizontal rows and vertical columns of a table in order of their increasing atomic weights in such a way that the elements with similar properties occupied the same vertical column or group. Mendeleev's system of classifying elements was more elaborate

than that of Lothar Meyer's. He fully recognized the significance of periodicity and used broader range of physical and chemical properties to classify the elements. In particular, Mendeleev relied on the similarities in the empirical formulas and properties of the compounds formed by the elements. He realized that some of the elements did not fit in with his scheme of classification if the order of atomic weight was strictly followed. He ignored the order of atomic weights, thinking that the atomic measurements might be incorrect, and placed the elements with similar properties together. For example, iodine with lower atomic weight than that of tellurium (Group VI) was placed in Group VII along with fluorine, chlorine, bromine because of similarities in properties (Fig. 3.1). At the same time, keeping his primary aim of arranging the elements of similar properties in the same group, he proposed that some of the elements were still undiscovered and, therefore, left several gaps in the table. For example, both gallium and germanium were unknown at the time Mendeleev published his Periodic Table. He left the gap under aluminium and a gap under silicon, and called these elements **Eka-Aluminium** and **Eka-Silicon.** Mendeleev predicted not only the existence of gallium and germanium, but also described some of their general physical properties. These elements were discovered later. Some of the properties predicted by Mendeleev for these elements and those found experimentally are listed in
Table 3.3.

Table 3.3 Mendeleev's Predictions for the Elements Eka-aluminium (Gallium) and Eka-silicon (Germanium)

Property	Eka-aluminium (predicted)	Gallium (found)	Eka-silicon (predicted)	Germanium (found)
Atomic weight	68	70	72	72.6
Density / (g/cm³)	5.9	5.94	5.5	5.36
Melting point /K	Low	302.93	High	1231
Formula of oxide	E_2O_3	Ga_2O_3	EO_2	GeO_2
Formula of chloride	ECl_3	$GaCl_3$	ECl_4	$GeCl_4$

The boldness of Mendeleev's quantitative predictions and their eventual success made him and his Periodic Table famous. Mendeleev's Periodic Table published in 1905 is shown in Fig. 3.1.

PERIODIC SYSTEM OF THE ELEMENTS IN GROUPS AND SERIES

SERIES	GROUPS OF ELEMENTS								
	0	I	II	III	IV	V	VI	VII	VIII
1	-	Hydrogen H 1.008	-	-					
2	Helium He 4.0	Lithium Li 7.03	Beryllium Be 9.1	Boron B 11.0	Carbon C 12.0	Nitrogen N 14.04	Oxygen O 16.00	Fluorine F 19.0	
3	Neon Ne 19.9	Sodium Na 23.5	Magnesium Mg 24.3	Aluminium Al 27.0	Silicon Si 28.4	Phosphorus P 31.0	Sulphur S 32.06	Chlorine Cl 35.45	
4	Argon Ar 38	Potassium K 39.1	Calcium Ca 40.1	Scandium Sc 44.1	Titanium Ti 48.1	Vanadium V 51.4	Chromium Cr 52.1	Manganese Mn 55.0	Iron Fe 55.9 Cobalt Co 59 Nickel Ni 59 (Cu)
5		Copper Cu 63.6	Zinc Zn 65.4	Gallium Ga 70.0	Germanium Ge 72.3	Arsenic As 75	Selenium Se 79	Bromine Br 79.95	
6	Krypton Kr 81.8	Rubidium Rb 85.4	Strontium Sr 87.6	Yttrium Y 89.0	Zirconium Zr 90.6	Niobium Nb 94.0	Molybdenum Mo 96.0	-	Ruthenium Ru 101.7 Rhodium Rh 103.0 Palladium Pd 106.5 (Ag)
7		Silver Ag 107.9	Cadmium Cd 112.4	Indium In 114.0	Tin Sn 119.0	Antimony Sb 120.0	Tellurium Te 127.6	Iodine I 126.9	
8	Xenon Xe 128	Caesium Cs 132.9	Barium Ba 137.4	Lanthanum La 139	Cerium Ce 140	-	-	-	
9		-	-	-	-	-	-	-	
10	-	-	-	Ytterbium Yb 173	-	Tantalum Ta 183	Tungsten W 184	-	Osmium Os 191 Iridium Ir 193 Platinum Pt 194.9 (Au)
11		Gold Au 197.2	Mercury Hg 200.0	Thallium Tl 204.1	Lead Pb 206.9	Bismuth Bi 208	-	-	
12	-	-	Radium Ra 224	-	Thorium Th 232	-	Uranium U 239		
	R	R_2O	RO	R_2O_3	RO_2	R_2O_5	RO_3	R_2O_7	RO_4
					HIGHER GASEOUS HYDROGEN COMPOUNDS				
					RH_4	RH_3	RH_2	RH	

Fig. 3.1 Mendeleev's Periodic Table published earlier

3.3 MODERN PERIODIC LAW AND THE PRESENT FORM OF THE PERIODIC TABLE

We must bear in mind that when Mendeleev developed his **Periodic**

Table, chemists knew nothing about the internal structure of atom. However, the beginning of the 20th century witnessed profound developments in theories about sub-atomic particles. In 1913, the English physicist, Henry Moseley observed regularities in the characteristic X-ray spectra of the elements. A plot of $\sqrt{\nu}$ (where n is frequency of X-rays emitted) against atomic number (Z) gave a straight line and not the plot of $\sqrt{\nu}$ vs atomic mass. He thereby showed that the atomic number is a more fundamental property of an element than its atomic mass. **Mendeleev's Periodic Law** was, therefore, accordingly modified. This is known as the **Modern Periodic Law** and can be stated as :

The physical and chemical properties of the elements are periodic functions of their atomic numbers.

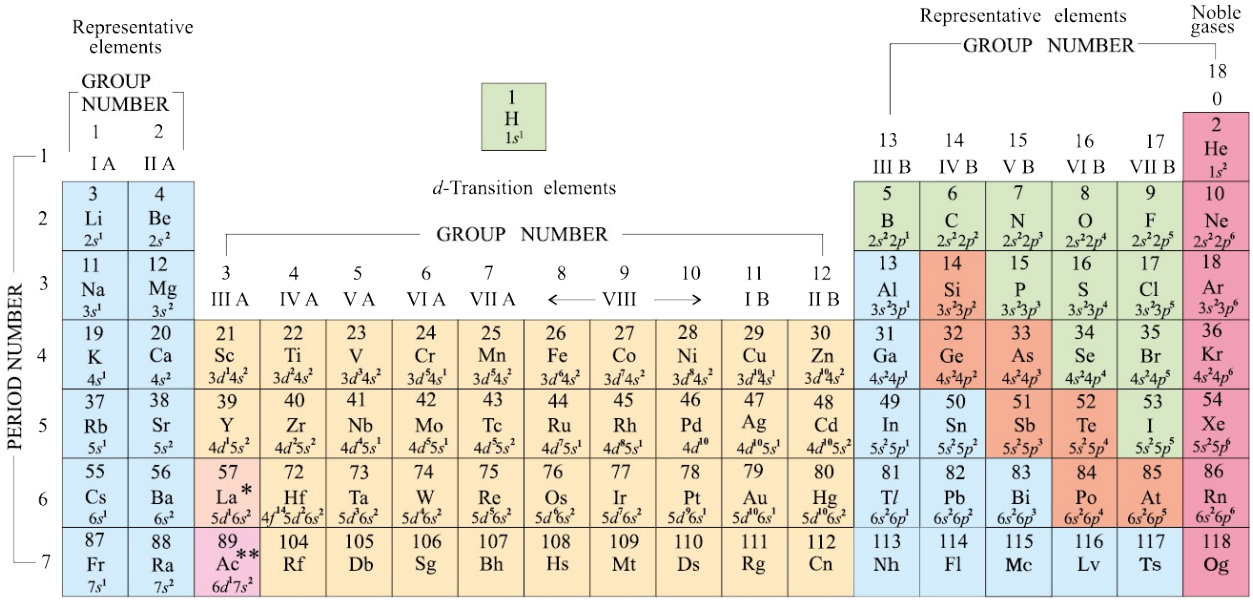
The **Periodic Law** revealed important analogies among the 94 naturally occurring elements (neptunium and plutonium like actinium and protoactinium are also found in pitch blende – an ore of uranium). It stimulated renewed interest in Inorganic Chemistry and has carried into the present with the creation of artificially produced short-lived elements.

You may recall that the atomic number is equal to the nuclear charge (i.e., number of protons) or the number of electrons in a neutral atom. It is then easy to visualize the significance of quantum numbers and electronic configurations in periodicity of elements. In fact, it is now recognized that the Periodic Law is essentially the consequence of the periodic variation in electronic configurations, which indeed determine the physical and chemical properties of elements and their compounds.

Numerous forms of Periodic Table have been devised from time to time. Some forms emphasise chemical reactions and valence, whereas others stress the electronic configuration of elements. A modern version, the so-called "**long form**" of the **Periodic Table** of the elements (Fig. 3.2), is the most convenient and widely used. The horizontal rows (which Mendeleev

called **series**) are called **periods** and the vertical columns, **groups**. Elements having similar outer electronic configurations in their atoms are arranged in vertical columns, referred to as **groups** or **families**. According to the recommendation of International Union of Pure and Applied Chemistry (IUPAC), the groups are numbered from 1 to 18 replacing the older notation of groups IA … VIIA, VIII, IB … VIIB and 0.

There are altogether seven periods. The period number corresponds to the highest principal quantum number (n) of the elements in the period. The first period contains 2 elements. The subsequent periods consists of 8, 8, 18, 18 and 32 elements, respectively. The seventh period is incomplete and like the sixth period would have a theoretical maximum (on the basis of quantum numbers) of 32 elements. In this form of the Periodic Table, 14 elements of both sixth and seventh periods (lanthanoids and actinoids, respectively) are placed in separate panels at the bottom*.



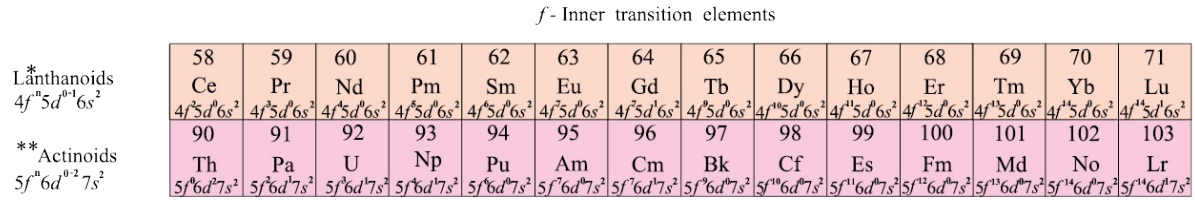


Fig. 3.2 Long form of the Periodic Table of the Elements with their atomic numbers and ground state outer electronic configurations. The groups are numbered 1-18 in accordance with the 1984 IUPAC recommendations. This notation replaces the old numbering scheme of IA–VIIA, VIII, IB–VIIB and 0 for the elements.

3.4 NOMENCLATURE OF ELEMENTS WITH ATOMIC NUMBERS > 100

The naming of the new elements had been traditionally the privilege of the discoverer (or discoverers) and the suggested name was ratified by the IUPAC. In recent years this has led to some controversy. The new elements with very high atomic numbers are so unstable that only minute quantities, sometimes only a few atoms of them are obtained. Their synthesis and characterisation, therefore, require highly sophisticated costly equipment and laboratory. Such work is carried out with competitive spirit only in some laboratories in the world. Scientists, before collecting the reliable data on the new element, at times get tempted to claim for its discovery. For example, both American and Soviet scientists claimed credit for discovering element 104. The Americans named it Rutherfordium whereas Soviets named it Kurchatovium. To avoid such problems, the IUPAC has made recommendation that until a new element's discovery is proved, and its name is officially recognised, a systematic nomenclature be derived directly from the atomic number of the element using the numerical roots for 0 and numbers 1-9. These are shown in Table 3.4. The roots are put together in order of digits which make up the atomic number and "ium" is added at the end. The IUPAC names for elements with Z above 100 are shown in Table 3.5.

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* *Glenn T. Seaborg's work in the middle of the 20th century starting with the discovery of plutonium in 1940, followed by those of all the transuranium elements from 94 to 102 led to reconfiguration of the periodic table placing the actinoids below the lanthanoids. In 1951, Seaborg*

was awarded the Nobel Prize in chemistry for his work. Element 106 has been named Seaborgium (Sg) in his honour.

Table 3.4 Notation for IUPAC Nomenclature of Elements

Digit	Name	Abbreviation
0	nil	n
1	un	u
2	bi	b
3	tri	t
4	quad	q
5	pent	p
6	hex	h
7	sept	s
8	oct	o
9	enn	e

Table 3.5 Nomenclature of Elements with Atomic Number Above 100

Atomic Number	Name according to IUPAC nomenclature	Symbol	IUPAC Official Name	IUPAC Symbol
101	Unnilunium	Unu	Mendelevium	Md
102	Unnilbium	Unb	Nobelium	No
103	Unniltrium	Unt	Lawrencium	Lr
104	Unnilquadium	Unq	Rutherfordium	Rf
105	Unnilpentium	Unp	Dubnium	Db
106	Unnilhexium	Unh	Seaborgium	Sg
107	Unnilseptium	Uns	Bohrium	Bh
108	Unniloctium	Uno	Hassium	Hs
109	Unnilennium	Une	Meitnerium	Mt
110	Ununnillium	Uun	Darmstadtium	Ds
111	Unununnium	Uuu	Rontgenium	Rg
112	Ununbium	Uub	Copernicium	Cn
113	Ununtrium	Uut	Nihonium	Nh
114	Ununquadium	Uuq	Flerovium	Fl
115	Ununpentium	Uup	Moscovium	Mc
116	Ununhexium	Uuh	Livermorium	Lv
117	Ununseptium	Uus	Tennessine	Ts
118	Ununoctium	Uuo	Oganesson	Og

Thus, the new element first gets a temporary name, with symbol consisting of three letters. Later permanent name and symbol are given by a vote of IUPAC representatives from each country. The permanent name might reflect the country (or state of the country) in which the element was discovered, or pay tribute to a notable scientist. As of now, elements with atomic numbers up to 118 have been discovered. Official names of all elements have been announced by IUPAC.

Problem 3.1

What would be the IUPAC name and symbol for the element with atomic number 120?

Solution

From Table 3.4, the roots for 1, 2 and 0 are un, bi and nil, respectively. Hence, the symbol and the name respectively are Ubn and unbinilium.

3.5 ELECTRONIC CONFIGURATIONS OF ELEMENTS AND THE PERIODIC TABLE

In the preceding unit we have learnt that an electron in an atom is characterised by a set of four quantum numbers, and the principal quantum number (n) defines the main energy level known as **shell**. We have also studied about the filling of electrons into different subshells, also referred to as **orbitals** (s, p, d, f) in an atom. The distribution of electrons into orbitals of an atom is called its **electronic configuration**. An element's location in the Periodic Table reflects the quantum numbers of the last orbital filled. In this section we will observe a direct connection between the electronic configurations of the elements and the long form of the Periodic Table.

(a) Electronic Configurations in Periods

The period indicates the value of n for the outermost or valence shell. In other words, successive period in the Periodic Table is associated with the filling of the next higher principal energy level (n = 1, n = 2, etc.). It can be readily seen that the number of elements in each period is twice the number of atomic **orbitals** available in the energy level that is being filled. The first period (n = 1) starts with the filling of the lowest level (1s) and therefore has two elements — hydrogen (ls^1) and helium (ls^2) when the first shell (K) is completed. The second period (n = 2) starts with lithium and the third electron enters the 2s orbital. The next element, beryllium has four electrons and has the electronic configuration $1s^2 2s^2$. Starting from the next element boron, the 2p orbitals are filled with electrons when the L shell is completed at neon ($2s^2 2p^6$). Thus there are 8 elements in the second period. The third period (n = 3) begins at sodium, and the added electron enters a 3s orbital. Successive filling of 3s and 3p orbitals gives rise to the third period of 8 elements from sodium to argon. The fourth period (n = 4) starts at potassium, and the added electrons fill up the 4s orbital. Now you may note that before the 4p orbital is filled, filling up of 3d orbitals becomes energetically favourable and we come across the so called 3d **transition series** of elements. This starts from scandium (Z = 21) which has the electronic configuration $3d^1 4s^2$. The 3d orbitals are filled at zinc (Z=30) with electronic configuration $3d^{10} 4s^2$. The fourth period ends at krypton with the filling up of the 4p orbitals. Altogether we have 18 elements in this fourth period. The fifth period (n = 5) beginning with rubidium is similar to the fourth period and contains the 4d **transition series** starting at yttrium (Z = 39). This period ends at xenon with the filling up of the 5p orbitals. The sixth period (n = 6) contains 32 elements and successive electrons enter 6s, 4f, 5d and 6p orbitals, in the order — filling up of the 4f orbitals begins with cerium (Z = 58) and ends at lutetium (Z = 71) to give the 4f-**inner**

transition series which is called the **lanthanoid series**. The seventh period (n = 7) is similar to the sixth period with the successive filling up of the 7s, 5f, 6d and 7p orbitals and includes most of the man-made radioactive elements. This period will end at the element with atomic number 118 which would belong to the noble gas family. Filling up of the 5f orbitals after actinium (Z = 89) gives the 5f-**inner transition series** known as the **actinoid series**. The 4f- and 5f-**inner transition series** of elements are placed separately in the Periodic Table to maintain its structure and to preserve the principle of classification by keeping elements with similar properties in a single column.

Problem 3.2

How would you justify the presence of 18 elements in the 5^{th} period of the Periodic Table?

Solution

When n = 5, l = 0, 1, 2, 3. The order in which the energy of the available orbitals 4d, 5s and 5p increases is 5s < 4d < 5p. The total number of orbitals available are 9. The maximum number of electrons that can be accommodated is 18; and therefore 18 elements are there in the 5^{th} period.

(b) Groupwise Electronic Configurations

Elements in the same vertical column or group have similar valence shell electronic configurations, the same number of electrons in the outer orbitals, and similar properties. For example, the Group 1 elements (alkali metals) all have ns^1 valence shell electronic configuration as shown below.

Thus it can be seen that the properties of an element have periodic dependence upon its atomic number and not on relative atomic mass.

3.6 ELECTRONIC CONFIGURATIONS AND TYPES OF

ELEMENTS: s-, p-, d-, f- BLOCKS

The aufbau (build up) principle and the electronic configuration of atoms provide a theoretical foundation for the periodic classification. The elements in a vertical column of the Periodic Table constitute a group or family and exhibit similar chemical behaviour. This similarity arises because these elements have the same number and same distribution of electrons in their outermost orbitals. We can classify the elements into four blocks viz., s**-block,** p**-block,** d**-block** and f**-block** depending on the type of atomic orbitals that are being filled with electrons. This is illustrated in Fig. 3.3. We notice two exceptions to this categorisation. Strictly, helium belongs to the s-block but its positioning in the p-block along with other group 18 elements is justified because it has a completely filled valence shell ($1s^2$) and as a result, exhibits properties characteristic of other noble gases. The other exception is hydrogen. It has only one s-electron and hence can be placed in group 1 (alkali metals). It can also gain an electron to achieve a noble gas arrangement and hence it can behave similar to a group 17 (halogen family) elements. Because it is a special case, we shall place hydrogen separately at the top of the Periodic Table as shown in Fig. 3.2 and Fig. 3.3. We will briefly discuss the salient features of the four types of elements marked in the Periodic Table. More about these elements will be discussed later. During the description of their features certain terminology has been used which has been classified in section 3.7.

Atomic number	Symbol	Electronic configuration
3	Li	$1s^2 2s^1$ **(or)** [He]$2s^1$
11	Na	$1s^2 2s^2 2p^6 3s^1$ **(or)** [Ne]$3s^1$
19	K	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$ **(or)** [Ar]$4s^1$
37	Rb	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 5s^1$ **(or)** [Kr]$5s^1$
55	Cs	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^6 6s^1$ **(or)** [Xe]$6s^1$
87	Fr	[Rn]$7s^1$

3.6.1 The s-Block Elements

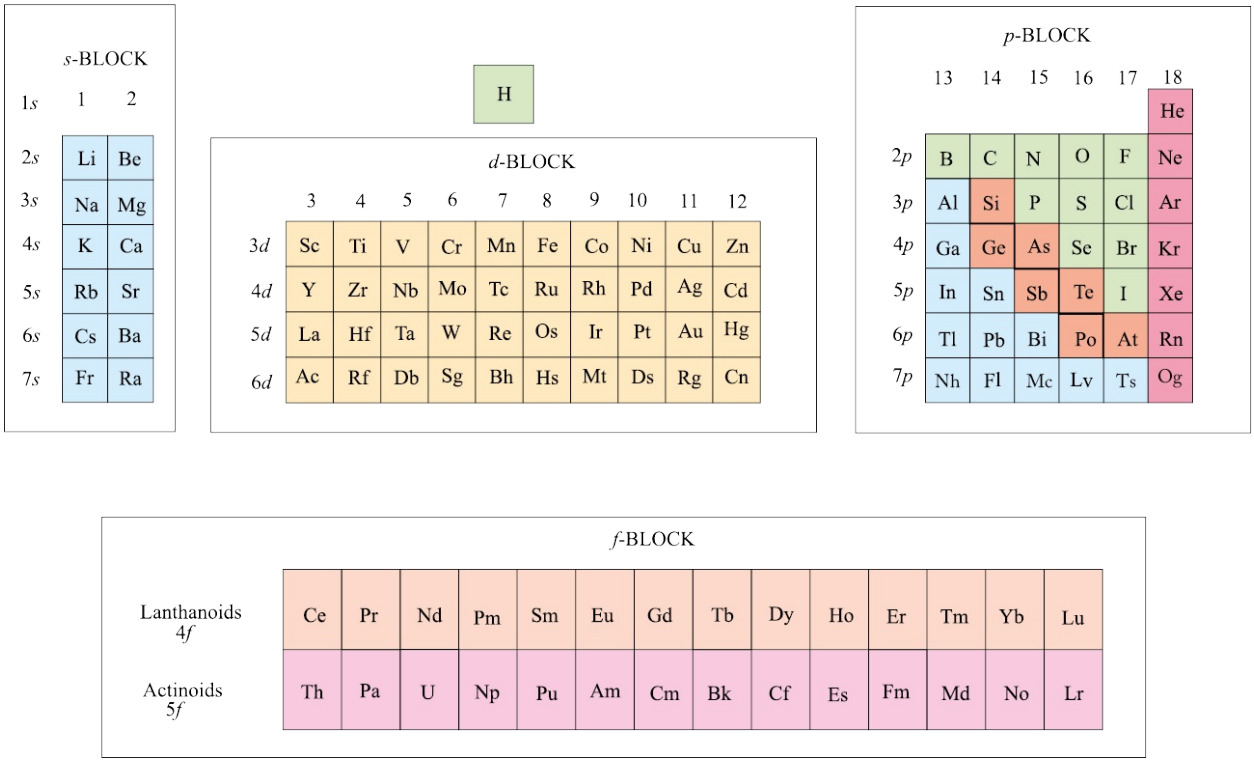


Fig. 3.3 The types of elements in the Periodic Table based on the orbitals that are being filled. Also shown is the broad division of elements into METALS ( ), NON-METALS ( ) and METALLOIDS ( ).

The elements of Group 1 (alkali metals) and Group 2 (alkaline earth metals) which have ns^1 and ns^2 outermost electronic configuration belong to the s-**Block Elements**. They are all reactive metals with low ionization enthalpies. They lose the outermost electron(s) readily to form 1+ ion (in the case of alkali metals) or 2+ ion (in the case of alkaline earth metals). The metallic character and the reactivity increase as we go down the group. Because of high reactivity they are never found pure in nature. The compounds of the s-block elements, with the exception of those of lithium and beryllium are predominantly ionic.

3.6.2 The p-Block Elements

The p-**Block Elements** comprise those belonging to Group 13 to 18 and these together with the s-**Block Elements** are called the **Representative Elements or Main Group Elements**. The outermost electronic configuration varies from ns^2np^1 to ns^2np^6 in each period. At the end of each period is a noble gas element with a closed valence shell ns^2np^6 configuration. All the orbitals in the valence shell of the **noble gases** are completely filled by electrons and it is very difficult to alter this stable arrangement by the addition or removal of electrons. The noble gases thus exhibit very low chemical reactivity. Preceding the noble gas family are two chemically important groups of non-metals. They are the **halogens** (Group 17) and the **chalcogens** (Group 16). These two groups of elements have highly negative electron gain enthalpies and readily add one or two electrons respectively to attain the stable noble gas configuration. The non-metallic character increases as we move from left to right across a period and metallic character increases as we go down the group.

3.6.3 The d-Block Elements (Transition Elements)

These are the elements of Group 3 to 12 in the centre of the Periodic Table. These are characterised by the filling of inner d orbitals by electrons and are therefore referred to as

d-**Block Elements**. These elements have the general outer electronic configuration (n-1) $d^{1-10}ns^{0-2}$. They are all metals. They mostly form coloured ions, exhibit variable valence (oxidation states), paramagnetism and oftenly used as catalysts. However, Zn, Cd and Hg which have the electronic configuration, (n-1) $d^{10}ns^2$ do not show most of the properties of transition elements. In a way, transition metals form a bridge between the chemically active metals of s-block elements and the less active elements of Groups 13 and 14 and thus take their familiar name **"Transition Elements"**.

3.6.4 The f-Block Elements (Inner-Transition Elements)

The two rows of elements at the bottom of the Periodic Table, called the **Lanthanoids,** Ce(Z = 58) – Lu(Z = 71) and **Actinoids**, Th (Z = 90) – Lr (Z = 103) are characterised by the outer electronic configuration $(n-2)f^{1-14}\ (n-1)d^{0-1}ns^2$. The last electron added to each element is filled in f- orbital. These two series of elements are hence called the **Inner-Transition Elements** (f-**Block Elements**). They are all metals. Within each series, the properties of the elements are quite similar. The chemistry of the early actinoids is more complicated than the corresponding lanthanoids, due to the large number of oxidation states possible for these actinoid elements. Actinoid elements are radioactive. Many of the actinoid elements have been made only in nanogram quantities or even less by nuclear reactions and their chemistry is not fully studied. The elements after uranium are called **Transuranium Elements**.

Problem 3.3

The elements Z = 117 and 120 have not yet been discovered. In which family / group would you place these elements and also give the electronic configuration in each case.

Solution

We see from Fig. 3.2, that element with Z = 117, would belong to the halogen family (Group 17) and the electronic configuration would be [Rn] $5f^{14}6d^{10}7s^27p^5$. The element with Z = 120, will be placed in Group 2 (alkaline earth metals), and will have the electronic configuration [Uuo]$8s^2$.

3.6.5 Metals, Non-metals and Metalloids

In addition to displaying the classification of elements into s-, p-, d-, and f-**blocks**, Fig. 3.3 shows another broad classification of elements based on their properties. The elements can be divided into **Metals** and **Non-**

Metals. Metals comprise more than 78% of all known elements and appear on the left side of the **Periodic Table**. Metals are usually solids at room temperature [mercury is an exception; gallium and caesium also have very low melting points (303K and 302K, respectively)]. Metals usually have high melting and boiling points. They are good conductors of heat and electricity. They are malleable (can be flattened into thin sheets by hammering) and ductile (can be drawn into wires). In contrast, non-metals are located at the top right hand side of the **Periodic Table**. In fact, in a horizontal row, the property of elements change from metallic on the left to non-metallic on the right. Non-metals are usually solids or gases at room temperature with low melting and boiling points (boron and carbon are exceptions). They are poor conductors of heat and electricity. Most non-metallic solids are brittle and are neither malleable nor ductile. The elements become more metallic as we go down a group; the non-metallic character increases as one goes from left to right across the **Periodic Table**. The change from metallic to non-metallic character is not abrupt as shown by the thick zig-zag line in Fig. 3.3. The elements (e.g., silicon, germanium, arsenic, antimony and tellurium) bordering this line and running diagonally across the **Periodic Table** show properties that are characteristic of both metals and non-metals. These elements are called **Semi-metals** or **Metalloids**.

Problem 3.4

Considering the atomic number and position in the periodic table, arrange the following elements in the increasing order of metallic character : Si, Be, Mg, Na, P.

Solution

Metallic character increases down a group and decreases along a period as we move from left to right. Hence the order of increasing metallic character is: P < Si < Be < Mg < Na.

3.7 PERIODIC TRENDS IN PROPERTIES OF ELEMENTS

There are many observable patterns in the physical and chemical properties of elements as we descend in a group or move across a period in the Periodic Table. For example, within a period, chemical reactivity tends to be high in Group 1 metals, lower in elements towards the middle of the table, and increases to a maximum in the Group 17 non-metals. Likewise within a group of representative metals (say alkali metals) reactivity increases on moving down the group, whereas within a group of non-metals (say halogens), reactivity decreases down the group. But why do the properties of elements follow these trends? And how can we explain periodicity? To answer these questions, we must look into the theories of atomic structure and properties of the atom. In this section we shall discuss the periodic trends in certain physical and chemical properties and try to explain them in terms of number of electrons and energy levels.

3.7.1 Trends in Physical Properties

There are numerous physical properties of elements such as melting and boiling points, heats of fusion and vaporization, energy of atomization, etc. which show periodic variations. However, we shall discuss the periodic trends with respect to atomic and ionic radii, ionization enthalpy, electron gain enthalpy and electronegativity.

(a) Atomic Radius

You can very well imagine that finding the size of an atom is a lot more complicated than measuring the radius of a ball. Do you know why? Firstly, because the size of an atom

(~ 1.2 Å i.e., 1.2×10^{-10} m in radius) is very small. Secondly, since the electron cloud surrounding the atom does not have a sharp boundary, the determination of the atomic size cannot be precise. In other words, there is no practical way by which the size of an individual atom can be

measured. However, an estimate of the atomic size can be made by knowing the distance between the atoms in the combined state. One practical approach to estimate the size of an atom of a non-metallic element is to measure the distance between two atoms when they are bound together by a single bond in a covalent molecule and from this value, the "**Covalent Radius**" of the element can be calculated. For example, the bond distance in the chlorine molecule (Cl_2) is 198 pm and half this distance (99 pm), is taken as the atomic radius of chlorine. For metals, we define the term "**Metallic Radius"** which is taken as half the internuclear distance separating the metal cores in the metallic crystal. For example, the distance between two adjacent copper atoms in solid copper is 256 pm; hence the metallic radius of copper is assigned a value of 128 pm. For simplicity, in this book, we use the term **Atomic Radius** to refer to both covalent or metallic radius depending on whether the element is a non-metal or a metal. Atomic radii can be measured by X-ray or other spectroscopic methods.

The atomic radii of a few elements are listed in Table 3.6 . Two trends are obvious. We can explain these trends in terms of nuclear charge and energy level. The atomic size generally decreases across a period as illustrated in Fig. 3.4(a) for the elements of the second period. It is because within the period the outer electrons are in the same valence shell and the effective nuclear charge increases as the atomic number increases resulting in the increased attraction of electrons to the nucleus. Within a family or vertical column of the **periodic table**, the atomic radius increases regularly with atomic number as illustrated in Fig. 3.4(b). For alkali metals and halogens, as we descend the groups, the principal quantum number (n) increases and the valence electrons are farther from the nucleus. This happens because the inner energy levels are filled with electrons, which serve to shield the outer electrons from the pull of the

nucleus. Consequently the size of the atom increases as reflected in the atomic radii.

Note that the atomic radii of noble gases are not considered here. Being monoatomic, their (non-bonded radii) values are very large. In fact radii of noble gases should be compared not with the covalent radii but with the van der Waals radii of other elements.

Table 3.6(a) Atomic Radii/pm Across the Periods

Atom (Period II)	**Li**	**Be**	**B**	**C**	**N**	**O**	**F**
Atomic radius	152	111	88	77	74	66	64
Atom (Period III)	**Na**	**Mg**	**Al**	**Si**	**P**	**S**	**Cl**
Atomic radius	186	160	143	117	110	104	99

Table 3.6(b) Atomic Radii/pm Down a Family

Atom (Group I)	**Atomic Radius**	**Atom (Group 17)**	**Atomic Radius**
Li	152	**F**	64
Na	186	**Cl**	99
K	231	**Br**	114
Rb	244	**I**	133
Cs	262	**At**	140

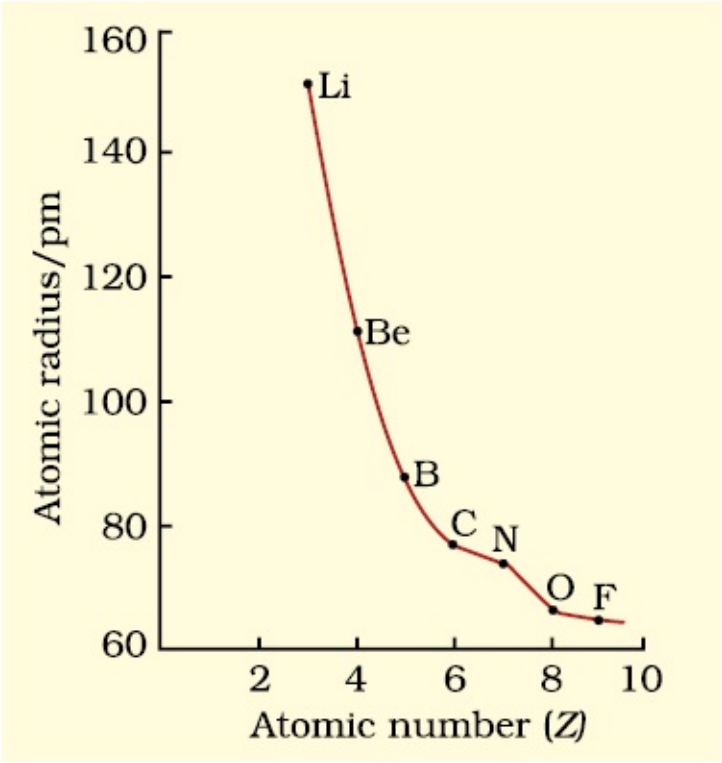


Fig. 3.4 (a) Variation of atomic radius with atomic number across the second period

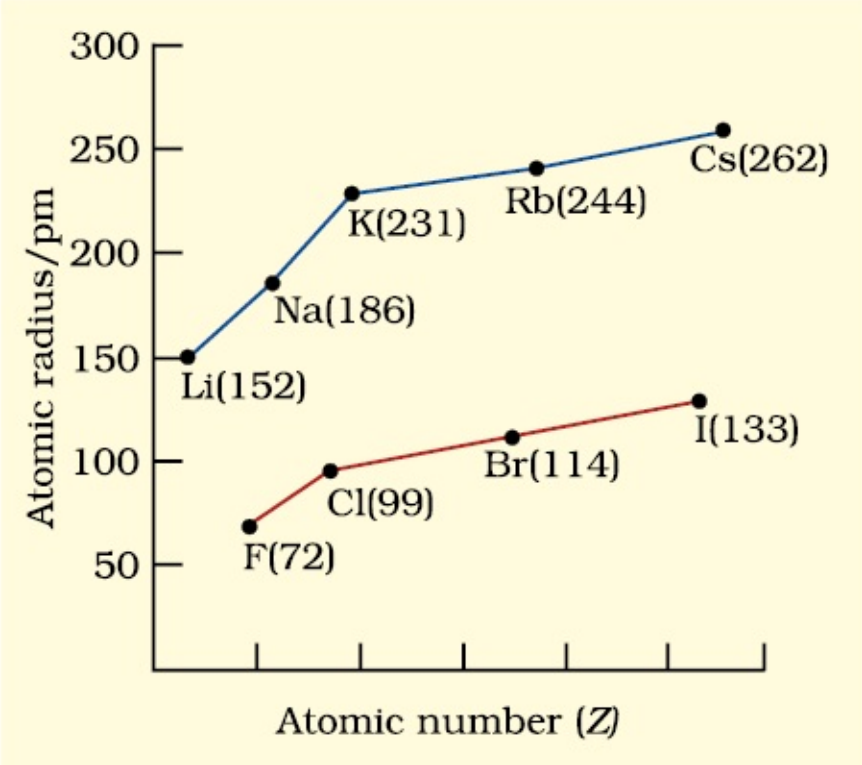


Fig. 3.4 (b) Variation of atomic radius with atomic number for alkali metals and halogens

(b) Ionic Radius

The removal of an electron from an atom results in the formation of a **cation**, whereas gain of an electron leads to an **anion**. The ionic radii can be estimated by measuring the distances between cations and anions in ionic crystals. In general, the ionic radii of elements exhibit the same trend as the atomic radii. A cation is smaller than its parent atom because it has fewer electrons while its nuclear charge remains the same. The size of an anion will be larger than that of the parent atom because the addition of one or more electrons would result in increased repulsion among the electrons and a decrease in effective nuclear charge. For example, the ionic radius of fluoride ion (F^-) is 136 pm whereas the atomic radius of fluorine is only 64 pm. On the other hand, the atomic radius of sodium is 186 pm compared to the ionic radius of 95 pm for Na^+.

When we find some atoms and ions which contain the same number of electrons, we call them **isoelectronic species***. For example,

O^{2-}, F^-, Na^+ and Mg^{2+} have the same number of electrons (10). Their radii would be different because of their different nuclear charges. The cation with the greater positive charge will have a smaller radius because of the greater attraction of the electrons to the nucleus. Anion with the greater negative charge will have the larger radius. In this case, the net repulsion of the electrons will outweigh the nuclear charge and the ion will expand in size.

Problem 3.5

Which of the following species will have the largest and the smallest size? Mg, Mg^{2+}, Al, Al^{3+}.

Solution

Atomic radii decrease across a period. Cations are smaller than their parent atoms. Among isoelectronic species, the one with the larger positive nuclear charge will have a smaller radius.

Hence the largest species is Mg; the smallest one is Al^{3+}.

(c) Ionization Enthalpy

A quantitative measure of the tendency of an element to lose electron is given by its **Ionization Enthalpy**. It represents the energy required to remove an electron from an isolated gaseous atom (X) in its ground state. In other words, the first ionization enthalpy for an element X is the enthalpy change (Δi H) for the reaction depicted in equation 3.1.

$$X(g) \rightarrow X^{+}(g) + e^{-} \qquad (3.1)$$

The ionization enthalpy is expressed in units of kJ mol^{-1}. We can define the second ionization enthalpy as the energy required to remove the second most loosely bound electron; it is the energy required to carry out the reaction shown in equation 3.2.

$$X^{+}(g) \rightarrow X^{2+}(g) + e^{-} \quad (3.2)$$

Energy is always required to remove electrons from an atom and hence ionization enthalpies are always positive. The second ionization enthalpy will be higher than the first ionization enthalpy because it is more difficult to remove an electron from a positively charged ion than from a neutral atom. In the same way the third ionization enthalpy will be higher than the second and so on. The term “ionization enthalpy”, if not qualified, is taken as the first ionization enthalpy.

** Two or more species with same number of atoms, same number of valence electrons and same structure, regardless of the nature of elements involved.*

The first ionization enthalpies of elements having atomic numbers up to 60 are plotted in Fig. 3.5. The periodicity of the graph is quite striking. You will find maxima at the noble gases which have closed electron shells and very stable electron configurations. On the other hand, minima occur at the alkali metals and their low ionization enthalpies can be correlated with their high reactivity. In addition, you will notice two trends the first ionization enthalpy generally increases as we go across a period and decreases as we descend in a group. These trends are illustrated in Figs. 3.6(a) and 3.6(b) respectively for the elements of the second period and the first group of the periodic table. You will appreciate that the ionization enthalpy and atomic radius are closely related properties. To understand these trends, we have to consider two factors : (i) the attraction of electrons towards the nucleus, and (ii) the repulsion of electrons from each other. The effective nuclear charge experienced by a valence electron in an atom will be less than the actual charge on the nucleus because of **“shielding”** or **“screening”** of the valence electron from the nucleus by the intervening core electrons. For example, the 2s electron in lithium is shielded from the nucleus by the inner core of 1s electrons. As a result, the valence electron experiences a net positive charge which is less than the actual charge of +3. In general, shielding is effective when the orbitals in the inner shells are completely filled. This situation occurs in the case of alkali metals which have single outermost ns-electron preceded by a noble gas electronic configuration.

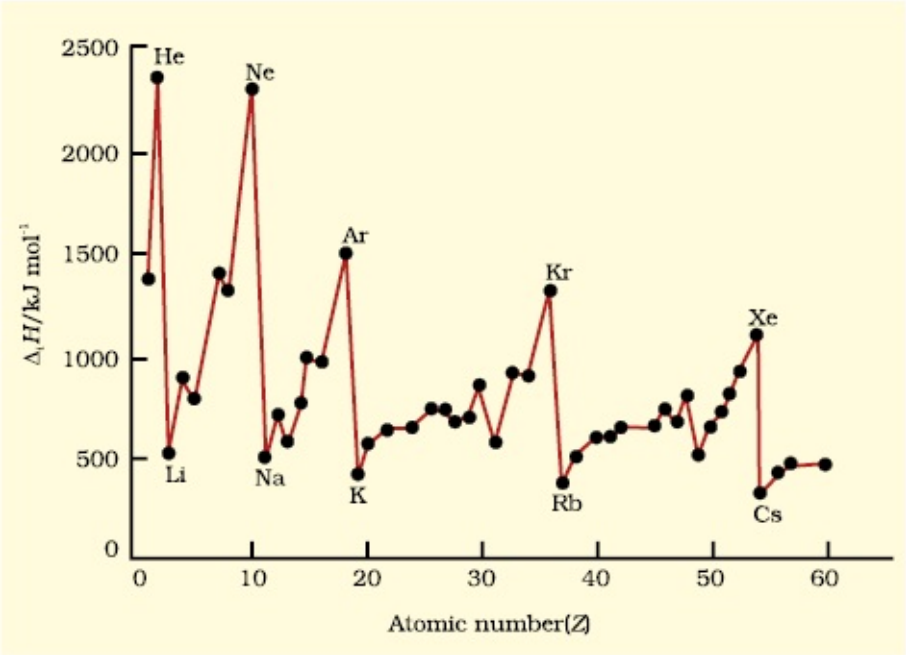
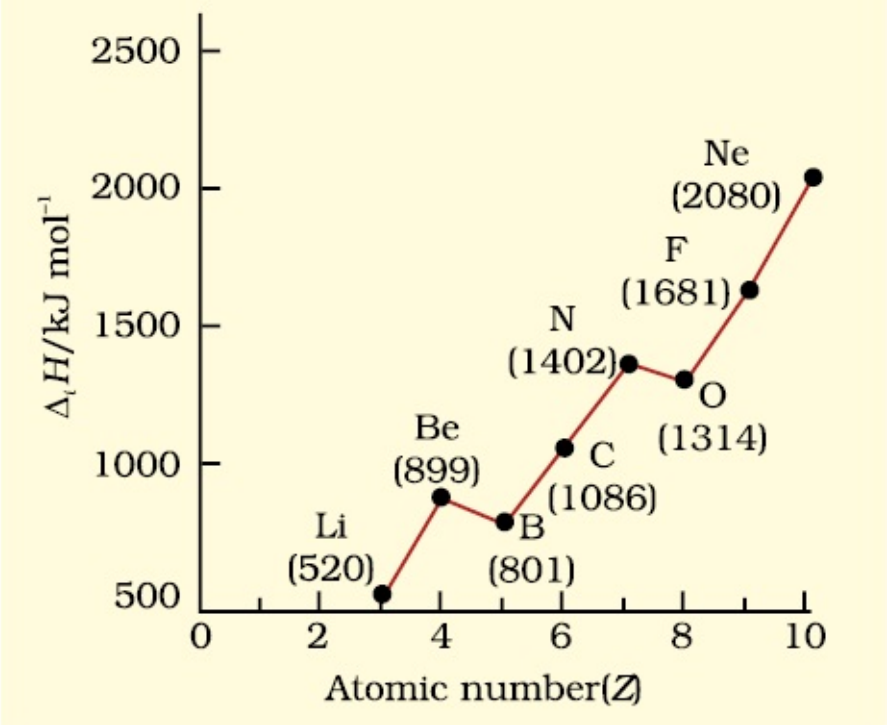
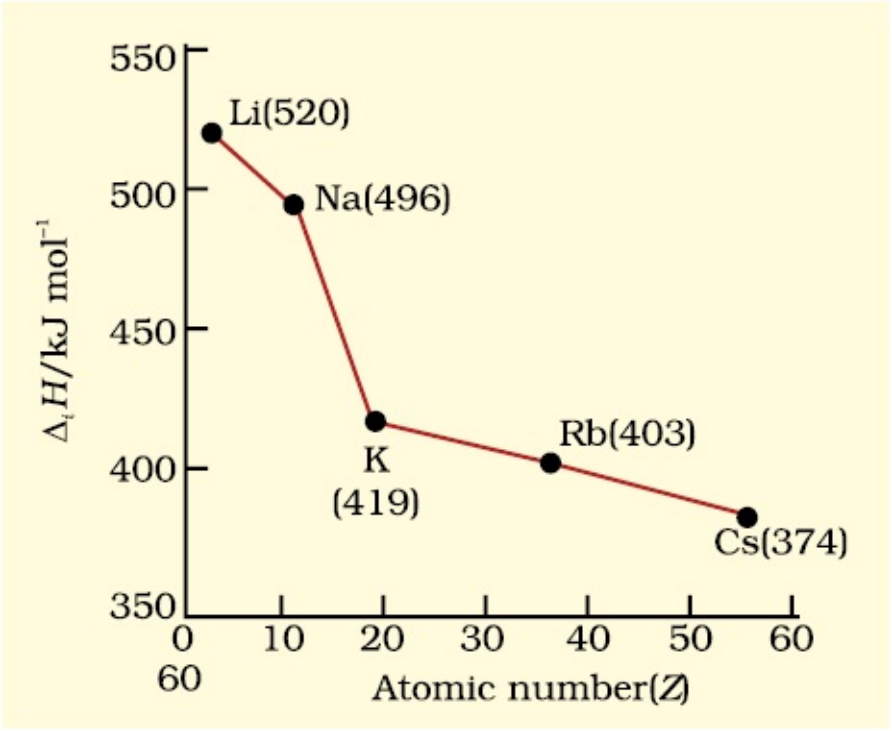


Fig. 3.5 Variation of first ionization enthalpies (∆iH) with atomic number for elements with Z = 1 to 60



3.6 (a)



3.6 (b)

Fig. 3.6(a) First ionization enthalpies (∆iH) of elements of the second period as a function of atomic number (Z) and Fig. 3.6(b) ∆iH of alkali metals as a function of Z.

When we move from lithium to fluorine across the second period, successive electrons are added to orbitals in the same principal quantum level and the shielding of the nuclear charge by the inner core of electrons does not increase very much to compensate for the increased attraction of the electron to the nucleus. Thus, across a period, increasing nuclear charge outweighs the shielding. Consequently, the outermost electrons are held more and more tightly and the ionization enthalpy increases across a period. As we go down a group, the outermost electron being increasingly farther from the nucleus, there is an increased shielding of the nuclear charge by the electrons in the inner levels. In this case, increase in shielding outweighs the increasing nuclear charge and the removal of the outermost electron requires less energy down a group. From Fig. 3.6(a), you will also notice that the first ionization enthalpy of boron (Z = 5) is slightly less than that of beryllium (Z = 4) even though the

former has a greater nuclear charge. When we consider the same principal quantum level, an s-electron is attracted to the nucleus more than a p-electron. In beryllium, the electron removed during the ionization is an s-electron whereas the electron removed during ionization of boron is a p-electron. The penetration of a 2s-electron to the nucleus is more than that of a 2p-electron; hence the 2p electron of boron is more shielded from the nucleus by the inner core of electrons than the 2s electrons of beryllium. Therefore, it is easier to remove the 2p-electron from boron compared to the removal of a 2s- electron from beryllium. Thus, boron has a smaller first ionization enthalpy than beryllium. Another "anomaly" is the smaller first ionization enthalpy of oxygen compared to nitrogen. This arises because in the nitrogen atom, three 2p-electrons reside in different atomic orbitals (Hund's rule) whereas in the oxygen atom, two of the four 2p-electrons must occupy the same 2p-orbital resulting in an increased electron-electron repulsion. Consequently, it is easier to remove the fourth 2p-electron from oxygen than it is, to remove one of the three 2p-electrons from nitrogen.

Problem 3.6

The first ionization enthalpy ($\Delta_i H$) values of the third period elements, Na, Mg and Si are respectively 496, 737 and 786 kJ mol^{-1}. Predict whether the first $\Delta_i H$ value for Al will be more close to 575 or 760 kJ mol^{-1} ? Justify your answer.

Solution

It will be more close to 575 kJ mol^{-1}. The value for Al should be lower than that of Mg because of effective shielding of 3p electrons from the nucleus by 3s-electrons.

(d) Electron Gain Enthalpy

When an electron is added to a neutral gaseous atom (X) to convert it into a negative ion, the enthalpy change accompanying the process is defined as the **Electron Gain Enthalpy** ($\Delta_{eg}H$). Electron gain enthalpy provides a measure of the ease with which an atom adds an electron to form anion as represented by equation 3.3.

$$X(g) + e^- \rightarrow X^-(g) \qquad (3.3)$$

Depending on the element, the process of adding an electron to the atom can be either endothermic or exothermic. For many elements energy is released when an electron is added to the atom and the electron gain enthalpy is negative. For example, group 17 elements (the halogens) have very high negative electron gain enthalpies because they can attain stable noble gas electronic configurations by picking up an electron. On the other hand, noble gases have large positive electron gain enthalpies because the electron has to enter the next higher principal quantum level leading to a very unstable electronic configuration. It may be noted that electron gain enthalpies have large negative values toward the upper right of the periodic table preceding the noble gases.

Table 3.7 Electron Gain Enthalpies* / (kJ mol–1) of Some Main Group Elements

Group 1	$\Delta_{eg}H$	Group 16	$\Delta_{eg}H$	Group 17	$\Delta_{eg}H$	Group 0	$\Delta_{eg}H$
H	– 73					He	+ 48
Li	– 60	O	– 141	F	– 328	Ne	+ 116
Na	– 53	S	– 200	Cl	– 349	Ar	+ 96
K	– 48	Se	– 195	Br	– 325	Kr	+ 96
Rb	– 47	Te	– 190	I	– 295	Xe	+ 77
Cs	– 46	Po	– 174	At	– 270	Rn	+ 68

The variation in electron gain enthalpies of elements is less systematic than for ionization enthalpies. As a general rule, electron gain enthalpy becomes more negative with increase in the atomic number across a

period. The effective nuclear charge increases from left to right across a period and consequently it will be easier to add an electron to a smaller atom since the added electron on an average would be closer to the positively charged nucleus. We should also expect electron gain enthalpy to become less negative as we go down a group because the size of the atom increases and the added electron would be farther from the nucleus. This is generally the case (Table 3.7). However, electron gain enthalpy of O or F is less negative than that of the succeeding element. This is because when an electron is added to O or F, the added electron goes to the smaller n = 2 quantum level and suffers significant repulsion from the other electrons present in this level. For the n = 3 quantum level (S or Cl), the added electron occupies a larger region of space and the electron-electron repulsion is much less.

Problem 3.7

Which of the following will have the most negative electron gain enthalpy and which the least negative?

P, S, Cl, F.

Explain your answer.

Solution

Electron gain enthalpy generally becomes more negative across a period as we move from left to right. Within a group, electron gain enthalpy becomes less negative down a group. However, adding an electron to the 2p-orbital leads to greater repulsion than adding an electron to the larger 3p-orbital. Hence the element with most negative electron gain enthalpy is chlorine; the one with the least negative electron gain enthalpy is phosphorus.

(e) Electronegativity

A qualitative measure of the ability of an atom in a **chemical compound** to attract shared electrons to itself is called **electronegativity**. Unlike

ionization enthalpy and electron gain enthalpy, it is not a measureable quantity. However, a number of numerical scales of electronegativity of elements viz., Pauling scale, Mulliken-Jaffe scale, Allred-Rochow scale have been developed. The one which is the most widely used is the Pauling scale. Linus Pauling, an American scientist, in 1922 assigned arbitrarily a value of 4.0 to fluorine, the element considered to have the greatest ability to attract electrons. Approximate values for the electronegativity of a few elements are given in Table 3.8(a)

** In many books, the negative of the enthalpy change for the process depicted in equation 3.3 is defined as the ELECTRON AFFINITY (A_e) of the atom under consideration. If energy is released when an electron is added to an atom, the electron affinity is taken as positive, contrary to thermodynamic convention. If energy has to be supplied to add an electron to an atom, then the electron affinity of the atom is assigned a negative sign. However, electron affinity is defined as absolute zero and, therefore at any other temperature (T) heat capacities of the reactants and the products have to be taken into account in $\Delta_{eg}H = -A_e - 5/2\ RT$.*

The electronegativity of any given element is not constant; it varies depending on the element to which it is bound. Though it is not a measurable quantity, it does provide a means of predicting the nature of force that holds a pair of atoms together – a relationship that you will explore later.

Electronegativity generally increases across a period from left to right (say from lithium to fluorine) and decrease down a group (say from fluorine to astatine) in the periodic table. How can these trends be explained? Can the electronegativity be related to atomic radii, which tend to decrease across each period from left to right, but increase down each group ? The attraction between the outer (or valence) electrons and the nucleus increases as the atomic radius decreases in a period. The

electronegativity also increases. On the same account electronegativity values decrease with the increase in atomic radii down a group. The trend is similar to that of ionization enthalpy.

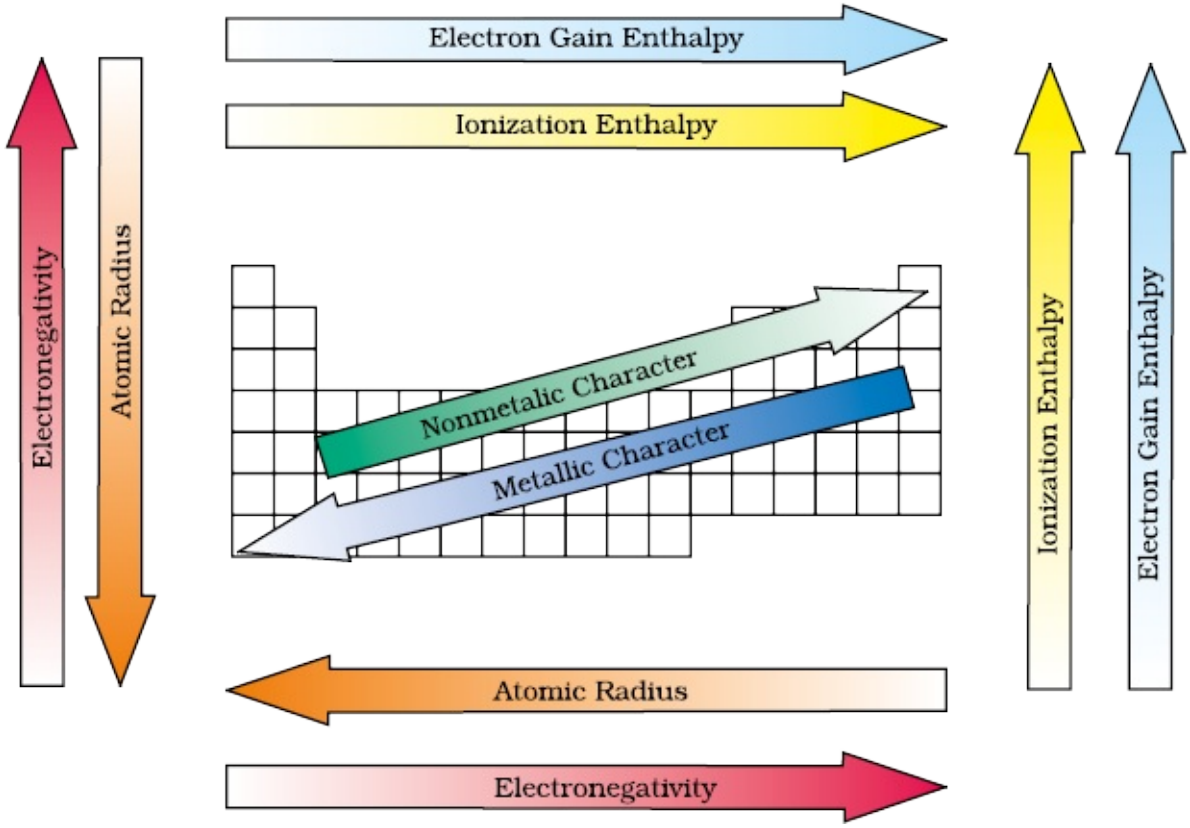


Fig. 3.7 The periodic trends of elements in the periodic table

Knowing the relationship between electronegativity and atomic radius, can you now visualise the relationship between electronegativity and non-metallic properties? Non-metallic elements have strong tendency to gain electrons. Therefore, electronegativity is directly related to that non-metallic properties of elements. It can be further extended to say that the electronegativity is inversely related to the metallic properties of elements. Thus, the increase in electronegativities across a period is accompanied by an increase in non-metallic properties (or decrease in metallic properties) of elements. Similarly, the decrease in electronegativity down a group is accompanied by a decrease in non-metallic properties (or increase in metallic properties) of elements.

All these periodic trends are summarised in figure 3.7.

Atom (Period II)	Li	Be	B	C	N	O	F
Electronegativity	1.0	1.5	2.0	2.5	3.0	3.5	4.0
Atom (Period III)	Na	Mg	Al	Si	P	S	Cl
Electronegativity	0.9	1.2	1.5	1.8	2.1	2.5	3.0

Table 3.8(a) Electronegativity Values (on Pauling scale) Across the Periods

Atom (Group I)	Electronegativity Value	Atom (Group 17)	Electronegativity Value
Li	1.0	F	4.0
Na	0.9	Cl	3.0
K	0.8	Br	2.8
Rb	0.8	I	2.5
Cs	0.7	At	2.2

Table 3.8(b) Electronegativity Values (on Pauling scale) Down a Family

3.7.2 Periodic Trends in Chemical Properties

Most of the trends in chemical properties of elements, such as diagonal relationships, inert pair effect, effects of lanthanoid contraction etc. will be dealt with along the discussion of each group in later units. In this section we shall study the periodicity of the valence state shown by elements and the anomalous properties of the second period elements (from lithium to fluorine).

(a) Periodicity of Valence or Oxidation States

The valence is the most characteristic property of the elements and can be understood in terms of their electronic configurations. The valence of representative elements is usually (though not necessarily) equal to the number of electrons in the outermost orbitals and / or equal to eight minus the number of outermost electrons as shown below.

Nowadays the term oxidation state is frequently used for valence. Consider the two oxygen containing compounds: OF_2 and Na_2O. The

order of electronegativity of the three elements involved in these compounds is F > O > Na. Each of the atoms of fluorine, with outer electronic configuration $2s^2 2p^5$, shares one electron with oxygen in the OF_2 molecule. Being highest electronegative element, fluorine is given oxidation state –1. Since there are two fluorine atoms in this molecule, oxygen with outer electronic configuration $2s^2 2p^4$ shares two electrons with fluorine atoms and thereby exhibits oxidation state +2. In Na_2O, oxygen being more electronegative accepts two electrons, one from each of the two sodium atoms and, thus, shows oxidation state –2. On the other hand sodium with electronic configuration $3s^1$ loses one electron to oxygen and is given oxidation state +1. Thus, the oxidation state of an element in a particular compound can be defined as the charge acquired by its atom on the basis of electronegative consideration from other atoms in the molecule.

Problem 3.8

Using the Periodic Table, predict the formulas of compounds which might be formed by the following pairs of elements; (a) silicon and bromine (b) aluminium and sulphur.

Solution

(a) Silicon is group 14 element with a valence of 4; bromine belongs to the halogen family with a valence of 1. Hence the formula of the compound formed would be $SiBr_4$.

(b) Aluminium belongs to group 13 with a valence of 3; sulphur belongs to group 16 elements with a valence of 2. Hence, the formula of the compound formed would be Al_2S_3.

Some periodic trends observed in the valence of elements (hydrides and oxides) are shown in Table 3.9. Other such periodic trends which occur in the chemical behaviour of the elements are discussed elsewhere in this book. There are many elements which exhibit variable valence. This is

particularly characteristic of transition elements and actinoids, which we shall study later.

Group	1	2	13	14	15	16	17	18
Number of valence electron	1	2	3	4	5	6	7	8
Valence	1	2	3	4	3,5	2,6	1,7	0,8

Table 3.9 Periodic Trends in Valence of Elements as shown by the Formulas of Their Compounds

Group	1	2	13	14	15	16	17
Formula of hydride	LiH NaH KH	CaH_2	B_2H_6 AlH_3	CH_4 SiH_4 GeH_4 SnH_4	NH_3 PH_3 AsH_3 SbH_3	H_2O H_2S H_2Se H_2Te	HF HCl HBr HI
Formula of oxide	Li_2O Na_2O K_2O	MgO CaO SrO BaO	B_2O_3 Al_2O_3 Ga_2O_3 In_2O_3	CO_2 SiO_2 GeO_2 SnO_2 PbO_2	N_2O_3, N_2O_5 P_4O_6, P_4O_{10} As_2O_3, As_2O_5 Sb_2O_3, Sb_2O_5 Bi_2O_3 –	 SO_3 SeO_3 TeO_3 –	– Cl_2O_7 – –

(b) Anomalous Properties of Second Period Elements

The first element of each of the groups 1 (lithium) and 2 (beryllium) and groups 13-17 (boron to fluorine) differs in many respects from the other members of their respective group. For example, lithium unlike other alkali metals, and beryllium unlike other alkaline earth metals, form compounds with pronounced covalent character; the other members of these groups predominantly form ionic compounds. In fact the behaviour of lithium and beryllium is more similar with the second element of the following group i.e., magnesium and aluminium, respectively. This sort of similarity is commonly referred to as **diagonal relationship** in the periodic properties.

Property	Element		
Metallic radius M/ pm	**Li**	**Be**	**B**
	152	111	88
	Na	**Mg**	**Al**
	186	160	143
Ionic radius M^+ / pm	**Li**	**Be**	
	76	31	
	Na	**Mg**	
	102	72	

What are the reasons for the different chemical behaviour of the first member of a group of elements in the s- and p-**blocks** compared to that of the subsequent members in the same group? The anomalous behaviour is attributed to their small size, large charge/radius ratio and high electronegativity of the elements. In addition, the first member of group has only four valence orbitals (2s and 2p) available for bonding, whereas the second member of the groups have nine valence orbitals (3s, 3p, 3d). As a consequence of this, the maximum covalency of the first member of each group is 4 (e.g., boron can only form $[BF_4]^-$, whereas the other members of the groups can expand their valence shell to accommodate more than four pairs of electrons e.g., aluminium $[AlF_4]^-$ forms). Furthermore, the first member of p-block elements displays greater ability to form pπ – pπ multiple bonds to itself (e.g., C = C, C ≡ C, N = N, N ≡ N) and to other second period elements (e.g., C = O, C = N, C ≡ N, N = O) compared to subsequent members of the same group.

Problem 3.9

Are the oxidation state and covalency of Al in $[AlCl(H_2O)_5]^{2+}$ same ?

Solution

No. The oxidation state of Al is +3 and the covalency is 6.

3.7.3 Periodic Trends and Chemical Reactivity

We have observed the periodic trends in certain fundamental properties such as atomic and ionic radii, ionization enthalpy, electron gain enthalpy and valence. We know by now that the periodicity is related to electronic configuration. That is, all chemical and physical properties are a manifestation of the electronic configuration of elements. We shall now try to explore relationships between these fundamental properties of elements with their chemical reactivity.

The atomic and ionic radii, as we know, generally decrease in a period from left to right. As a consequence, the ionization enthalpies generally increase (with some exceptions as outlined in section 3.7.1(a)) and electron gain enthalpies become more negative across a period. In other words, the ionization enthalpy of the extreme left element in a period is the least and the electron gain enthalpy of the element on the extreme right is the highest negative (note : noble gases having completely filled shells have rather positive electron gain enthalpy values). This results into high chemical reactivity at the two extremes and the lowest in the centre. Thus, the maximum chemical reactivity at the extreme left (among alkali metals) is exhibited by the loss of an electron leading to the formation of a cation and at the extreme right (among halogens) shown by the gain of an electron forming an anion. This property can be related with the reducing and oxidizing behaviour of the elements which you will learn later. However, here it can be directly related to the metallic and non-metallic character of elements. Thus, the metallic character of an element, which is highest at the extremely left decreases and the non-

metallic character increases while moving from left to right across the period. The chemical reactivity of an element can be best shown by its reactions with oxygen and halogens. Here, we shall consider the reaction of the elements with oxygen only. Elements on two extremes of a period easily combine with oxygen to form oxides. The normal oxide formed by the element on extreme left is the most basic (e.g., Na_2O), whereas that formed by the element on extreme right is the most acidic (e.g., Cl_2O_7). Oxides of elements in the centre are amphoteric (e.g., Al_2O_3, As_2O_3) or neutral (e.g., CO, NO, N_2O). Amphoteric oxides behave as acidic with bases and as basic with acids, whereas neutral oxides have no acidic or basic properties.

Problem 3.10

Show by a chemical reaction with water that Na_2O is a basic oxide and Cl_2O_7 is an acidic oxide.

Solution

Na_2O with water forms a strong base whereas Cl_2O_7 forms strong acid.

$Na_2O + H_2O \rightarrow 2NaOH$

$Cl_2O_7 + H_2O \rightarrow 2HClO_4$

Their basic or acidic nature can be qualitatively tested with litmus paper.

Among transition metals (3d series), the change in atomic radii is much smaller as compared to those of representative elements across the period. The change in atomic radii is still smaller among inner-transition metals

(4f series). The ionization enthalpies are intermediate between those of s- and p-blocks. As a consequence, they are less electropositive than group 1 and 2 metals.

In a group, the increase in atomic and ionic radii with increase in atomic number generally results in a gradual decrease in ionization enthalpies and a regular decrease (with exception in some third period elements as shown in section 3.7.1(d)) in electron gain enthalpies in the case of main group elements. Thus, the metallic character increases down the group and non-metallic character decreases. This trend can be related with their reducing and oxidizing property which you will learn later. In the case of transition elements, however, a reverse trend is observed. This can be explained in terms of atomic size and ionization enthalpy.

SUMMARY

In this Unit, you have studied the development of the **Periodic Law** and the **Periodic Table**. Mendeleev's **Periodic Table** was based on atomic masses. Modern **Periodic Table** arranges the elements in the order of their atomic numbers in seven horizontal rows (**periods**) and eighteen vertical columns (**groups** or **families**). Atomic numbers in a period are consecutive, whereas in a group they increase in a pattern. Elements of the same group have similar **valence shell** electronic configuration and, therefore, exhibit similar chemical properties. However, the elements of the same period have incrementally increasing number of electrons from left to right, and, therefore, have different valencies. Four types of elements can be recognized in the periodic table on the basis of their electronic configurations. These are s**-block,** p**-block,** d**-block** and f**-block** elements. **Hydrogen** with one electron in the 1s orbital occupies a unique position in the periodic table. **Metals** comprise more than seventy eight per cent of the known elements. **Non-metals**, which are located at the top of the periodic table, are less than twenty in number. Elements which lie at the border line between metals and non-metals (e.g., Si, Ge, As) are called **metalloids** or **semi-metals**. Metallic character increases with increasing atomic number in a group whereas decreases from left to right in a period. The physical and chemical properties of elements vary periodically with their atomic numbers.

Periodic trends are observed in **atomic sizes, ionization enthalpies, electron gain**

enthalpies, **electronegativity** and **valence.** The atomic radii decrease while going from left to right in a period and increase with atomic number in a group. Ionization enthalpies generally increase across a period and decrease down a group. Electronegativity also shows a similar trend. Electron gain enthalpies, in general, become more negative across a period and less negative down a group. There is some periodicity in valence, for example, among representative elements, the valence is either equal to the number of electrons in the outermost orbitals or eight minus this number. **Chemical reactivity** is highest at the two extremes of a period and is lowest in the centre. The reactivity on the left extreme of a period is because of the ease of electron loss (or low ionization enthalpy). Highly reactive elements do not occur in nature in free state; they usually occur in the combined form. Oxides formed of the elements on the left are basic and of the elements on the right are acidic in nature. Oxides of elements in the centre are amphoteric or neutral.

Exercises

3.1 What is the basic theme of organisation in the periodic table?

3.2 Which important property did Mendeleev use to classify the elements in his periodic table and did he stick to that?

3.3 What is the basic difference in approach between the Mendeleev's Periodic Law and the Modern Periodic Law?

3.4 On the basis of quantum numbers, justify that the sixth period of the periodic table should have 32 elements.

3.5 In terms of period and group where would you locate the element with $Z = 114$?

3.6 Write the atomic number of the element present in the third period and seventeenth group of the periodic table.

3.7 Which element do you think would have been named by

(i) Lawrence Berkeley Laboratory

(ii) Seaborg's group?

3.8 Why do elements in the same group have similar physical and chemical properties?

3.9 What does atomic radius and ionic radius really mean to you?

3.10 How do atomic radius vary in a period and in a group? How do you explain the variation?

3.11 What do you understand by isoelectronic species? Name a species that will be isoelectronic with each of the following atoms or ions.

(i) F– (ii) Ar (iii) Mg^{2+} (iv) Rb^{+}

3.12 Consider the following species :

N^{3-}, O^{2-}, F^{-}, Na^{+}, Mg^{2+} and Al^{3+}

(a) What is common in them?

(b) Arrange them in the order of increasing ionic radii.

3.13 Explain why cation are smaller and anions larger in radii than their parent atoms?

3.14 What is the significance of the terms — 'isolated gaseous atom' and 'ground state' while defining the ionization enthalpy and electron gain enthalpy?

Hint : Requirements for comparison purposes.

3.15 Energy of an electron in the ground state of the hydrogen atom is -2.18×10^{-18}J. Calculate the ionization enthalpy of atomic hydrogen in terms of

J mol^{-1}.

Hint: Apply the idea of mole concept to derive the answer.

3.16 Among the second period elements the actual ionization enthalpies are in the order Li < B < Be < C < O < N < F < Ne.

Explain why

(i) Be has higher $\Delta_i H$ than B

(ii) O has lower $\Delta_i H$ than N and F?

3.17 How would you explain the fact that the first ionization enthalpy of sodium is lower than that of magnesium but its second ionization enthalpy is higher than that of magnesium?

3.18 What are the various factors due to which the ionization enthalpy of

the main group elements tends to decrease down a group?

3.19 The first ionization enthalpy values (in kJ mol–1) of group 13 elements are :

B Al Ga In Tl

801 577 579 558 589

How would you explain this deviation from the general trend ?

3.20 Which of the following pairs of elements would have a more negative electron gain enthalpy?

(i) O or F (ii) F or Cl

3.21 Would you expect the second electron gain enthalpy of O as positive, more negative or less negative than the first? Justify your answer.

3.22 What is the basic difference between the terms electron gain enthalpy and electronegativity?

3.23 How would you react to the statement that the electronegativity of N on Pauling scale is 3.0 in all the nitrogen compounds?

3.24 Describe the theory associated with the radius of an atom as it

(a) gains an electron

(b) loses an electron

3.25 Would you expect the first ionization enthalpies for two isotopes of the same element to be the same or different? Justify your answer.

3.26 What are the major differences between metals and non-metals?

3.27 Use the periodic table to answer the following questions.

(a) Identify an element with five electrons in the outer subshell.

(b) Identify an element that would tend to lose two electrons.

(c) Identify an element that would tend to gain two electrons.

(d) Identify the group having metal, non-metal, liquid as well as gas at the room temperature.

3.28 The increasing order of reactivity among group 1 elements is Li < Na < K < Rb <Cs whereas that among group 17 elements is F > Cl > Br >

I. Explain.

3.29 Write the general outer electronic configuration of s-, p-, d- and f-block elements.

3.30 Assign the position of the element having outer electronic configuration

(i) ns2np4 for n=3 (ii) (n-1)d2ns2 for n=4, and (iii) (n-2) f 7 (n-1)d1ns2 for n=6, in the periodic table.

3.31 The first ($\Delta_i H_1$) and the second ($\Delta_i H_2$) ionization enthalpies (in kJ mol–1) and the (ΔegH) electron gain enthalpy (in kJ mol–1) of a few elements are given below:

Elements	ΔH_1	ΔH_2	$\Delta_{eg} H$
I	520	7300	–60
II	419	3051	–48
III	1681	3374	–328
IV	1008	1846	–295
V	2372	5251	+48
VI	738	1451	–40

Which of the above elements is likely to be :

(a) the least reactive element.

(b) the most reactive metal.

(c) the most reactive non-metal.

(d) the least reactive non-metal.

(e) the metal which can form a stable binary halide of the formula MX_2(X=halogen).

(f) the metal which can form a predominantly stable covalent halide of the formula MX (X=halogen)?

3.32 Predict the formulas of the stable binary compounds that would be formed by the combination of the following pairs of elements.

(a) Lithium and oxygen
(b) Magnesium and nitrogen
(c) Aluminium and iodine
(d) Silicon and oxygen
(e) Phosphorus and fluorine
(f) Element 71 and fluorine

3.33 In the modern periodic table, the period indicates the value of :
(a) atomic number
(b) atomic mass
(c) principal quantum number
(d) azimuthal quantum number.

3.34 Which of the following statements related to the modern periodic table is incorrect?
(a) The p-block has 6 columns, because a maximum of 6 electrons can occupy all the orbitals in a p-shell.
(b) The d-block has 8 columns, because a maximum of 8 electrons can occupy all the orbitals in a d-subshell.
(c) Each block contains a number of columns equal to the number of electrons that can occupy that subshell.
(d) The block indicates value of azimuthal quantum number (l) for the last subshell that received electrons in building up the electronic configuration.

3.35 Anything that influences the valence electrons will affect the chemistry of the element. Which one of the following factors does not affect the valence shell?
(a) Valence principal quantum number (n)
(b) Nuclear charge (Z)

(c) Nuclear mass
(d) Number of core electrons.

3.36 The size of isoelectronic species — F^-, Ne and Na^+ is affected by
(a) nuclear charge (Z)
(b) valence principal quantum number (n)
(c) electron-electron interaction in the outer orbitals
(d) none of the factors because their size is the same.

3.37 Which one of the following statements is incorrect in relation to ionization enthalpy?
(a) Ionization enthalpy increases for each successive electron.
(b) The greatest increase in ionization enthalpy is experienced on removal of electron from core noble gas configuration.
(c) End of valence electrons is marked by a big jump in ionization enthalpy.
(d) Removal of electron from orbitals bearing lower n value is easier than from orbital having higher n value.
3.38 Considering the elements B, Al, Mg, and K, the correct order of their metallic character is :
(a) B > Al > Mg > K
(b) Al > Mg > B > K
(c) Mg > Al > K > B
(d) K > Mg > Al > B
3.39 Considering the elements B, C, N, F, and Si, the correct order of their non-metallic character is :
(a) B > C > Si > N > F
(b) Si > C > B > N > F
(c) F > N > C > B > Si
(d) F > N > C > Si > B

3.40 Considering the elements F, Cl, O and N, the correct order of their chemical reactivity in terms of oxidizing property is :

(a) F > Cl > O > N

(b) F > O > Cl > N

(c) Cl > F > O > N

(d) O > F > N > Cl

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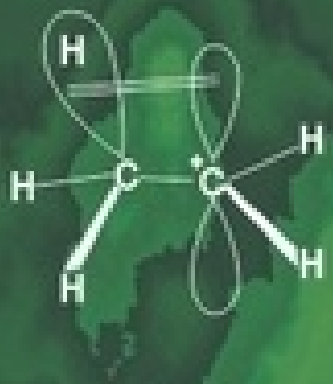
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Textbook for Class XI

Unit 4
CHEMICAL BONDING AND MOLECULAR STRUCTURE

Chemistry

Part I



11082CH04

Unit 4

CHEMICAL BONDING AND MOLECULAR STRUCTURE

Objectives

After studying this Unit, you will be able to

- understand KÖssel-Lewis approach to chemical bonding;
- explain the octet rule and its limitations, draw Lewis structures of simple molecules;
- explain the formation of different types of bonds;
- describe the VSEPR theory and predict the geometry of simple molecules;
- explain the valence bond approach for the formation of covalent bonds;
- predict the directional properties of covalent bonds;
- explain the different types of hybridisation involving s, p and d orbitals and draw shapes of simple covalent molecules;
- describe the molecular orbital theory of homonuclear diatomic molecules;
- explain the concept of hydrogen bond.

Scientists are constantly discovering new compounds, orderly arranging the facts about them, trying to explain with the existing knowledge, organising to modify the earlier views or evolve theories

for explaining the newly observed facts.

Matter is made up of one or different type of elements. Under normal conditions no other element exists as an independent atom in nature, except noble gases. However, a group of atoms is found to exist together as one species having characteristic properties. Such a group of atoms is called a molecule. Obviously there must be some force which holds these constituent atoms together in the molecules. **The attractive force which holds various constituents (atoms, ions, etc.) together in different chemical species is called a chemical bond.** Since the formation of chemical compounds takes place as a result of combination of atoms of various elements in different ways, it raises many questions. Why do atoms combine? Why are only certain combinations possible? Why do some atoms combine while certain others do not? Why do molecules possess definite shapes? To answer such questions different theories and concepts have been put forward from time to time. These are Kössel-Lewis approach, Valence Shell Electron Pair Repulsion (VSEPR) Theory, Valence Bond (VB) Theory and Molecular Orbital (MO) Theory. The evolution of various theories of valence and the interpretation of the nature of chemical bonds have closely been related to the developments in the understanding of the structure of atom, the electronic configuration of elements and the periodic table. Every system tends to be more stable and bonding is nature's way of lowering the energy of the system to attain stability.

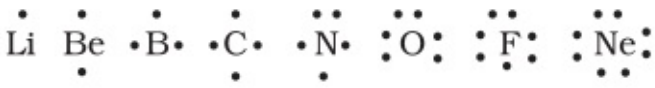
4.1 KÖssel-Lewis Approach to Chemical Bonding

In order to explain the formation of chemical bond in terms of electrons, a number of attempts were made, but it was only in 1916 when Kössel and Lewis succeeded independently in giving a satisfactory explanation. They were the first to provide some logical explanation of valence which was

based on the inertness of noble gases.

Lewis pictured the atom in terms of a positively charged 'Kernel' (the nucleus plus the inner electrons) and the outer shell that could accommodate a maximum of eight electrons. He, further assumed that these eight electrons occupy the corners of a cube which surround the 'Kernel'. Thus the single outer shell electron of sodium would occupy one corner of the cube, while in the case of a noble gas all the eight corners would be occupied. This octet of electrons, represents a particularly stable electronic arrangement. **Lewis postulated that atoms achieve the stable octet when they are linked by chemical bonds.** In the case of sodium and chlorine, this can happen by the transfer of an electron from sodium to chlorine thereby giving the Na^+ and Cl^- ions. In the case of other molecules like Cl_2, H_2, F_2, etc., the bond is formed by the sharing of a pair of electrons between the atoms. In the process each atom attains a **stable outer octet of electrons**.

Lewis Symbols: In the formation of a molecule, only the outer shell electrons take part in chemical combination and they are known as **valence electrons**. The inner shell electrons are well protected and are generally not involved in the combination process. G.N. Lewis, an American chemist introduced simple notations to represent valence electrons in an atom. These notations are called **Lewis symbols**. For example, the Lewis symbols for the elements of second period are as under:



Significance of Lewis Symbols : The number of dots around the symbol represents the number of valence electrons. This number of valence electrons helps to calculate the common or **group valence** of the element. The group valence of the elements is generally either equal

to the number of dots in Lewis symbols or 8 minus the number of dots or valence electrons.

Kössel, in relation to chemical bonding, drew attention to the following facts:

- In the periodic table, the highly electronegative halogens and the highly electropositive alkali metals are separated by the noble gases;
- The formation of a negative ion from a halogen atom and a positive ion from an alkali metal atom is associated with the gain and loss of an electron by the respective atoms;
- The negative and positive ions thus formed attain stable noble gas electronic configurations. The noble gases (with the exception of helium which has a duplet of electrons) have a particularly stable outer shell configuration of eight (octet) electrons, ns^2np^6.
- The negative and positive ions are stabilized by electrostatic attraction.

For example, the formation of NaCl from sodium and chlorine, according to the above scheme, can be explained as:

$Na \rightarrow Na^+ + e^-$

$[Ne]\ 3s^1 \quad [Ne]$

$Cl + e^- \rightarrow Cl^-$

$[Ne]\ 3s^2\ 3p^5 \quad [Ne]\ 3s^2\ 3p^6$ or [Ar]

$Na^+ + Cl^- \rightarrow$ NaCl or Na^+Cl^-

Similarly the formation of CaF_2 may be shown as:

$Ca \rightarrow Ca^{2+} + 2e^-$

$[Ar]4s^2 \quad [Ar]$

$F + e^- \rightarrow F^-$

$[He]\ 2s^2\ 2p^5 \quad [He]\ 2s^2\ 2p^6$ or [Ne]

$Ca^{2+} + 2F^{-} \rightarrow CaF_2$ or $Ca^{2+}(F^{-})_2$

The bond formed, as a result of the electrostatic attraction between the positive and negative ions was termed as the electrovalent bond. The electrovalence is thus equal to the number of unit charge(s) on the ion. Thus, calcium is assigned a positive electrovalence of two, while chlorine a negative electrovalence of one.

Kössel's postulations provide the basis for the modern concepts regarding ion-formation by electron transfer and the formation of ionic crystalline compounds. His views have proved to be of great value in the understanding and systematisation of the ionic compounds. At the same time he did recognise the fact that a large number of compounds did not fit into these concepts.

4.1.1 Octet Rule

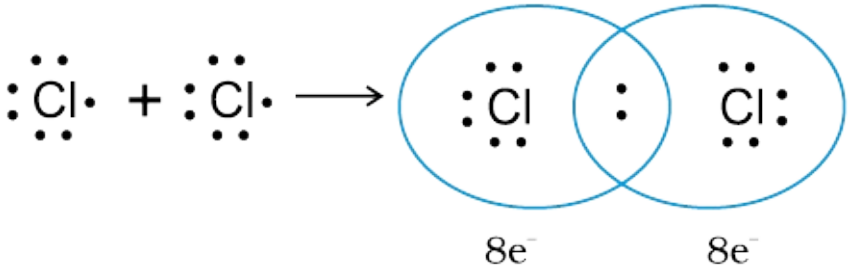
Kössel and Lewis in 1916 developed an important theory of chemical combination between atoms known as **electronic theory** of **chemical bonding**. According to this, atoms can combine either by transfer of valence electrons from one atom to another (gaining or losing) or by sharing of valence electrons in order to have an octet in their valence shells. This is known as **octet rule**.

4.1.2 Covalent Bond

Langmuir (1919) refined the Lewis postulations by abandoning the idea of the stationary cubical arrangement of the octet, and by introducing the term **covalent bond**. The Lewis-Langmuir theory can be understood by considering the formation of the chlorine molecule,Cl_2. The Cl atom with electronic configuration, $[Ne]3s^2\ 3p^5$, is one electron short of the argon configuration. The formation of the Cl_2 molecule can be understood in terms of the sharing of a pair of electrons between the two chlorine atoms, each chlorine atom contributing one electron to the shared pair. In

the process both chlorine atoms attain the outer shell octet of the nearest noble gas (i.e., argon).

or Cl – Cl

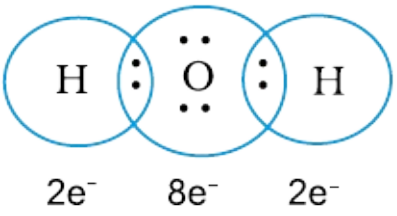


Covalent bond between two Cl atoms

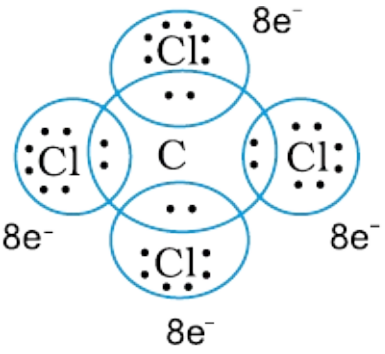
The dots represent electrons. Such structures are referred to as Lewis dot structures.

The Lewis dot structures can be written for other molecules also, in which the combining atoms may be identical or different. The important conditions being that:

- Each bond is formed as a result of sharing of an electron pair between the atoms.
- Each combining atom contributes at least one electron to the shared pair.
- The combining atoms attain the outer-shell noble gas configurations as a result of the sharing of electrons.
- Thus in water and carbon tetrachloride molecules, formation of covalent bonds can be represented as:



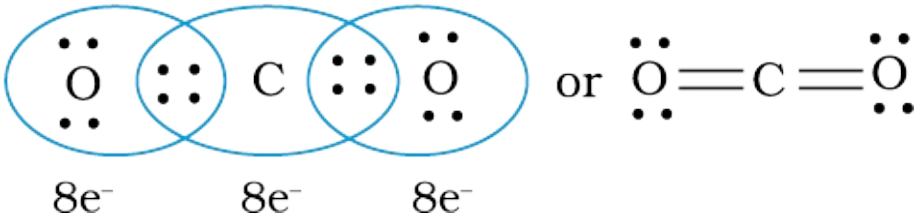
H atoms attain a duplet of electrons and O, the octet



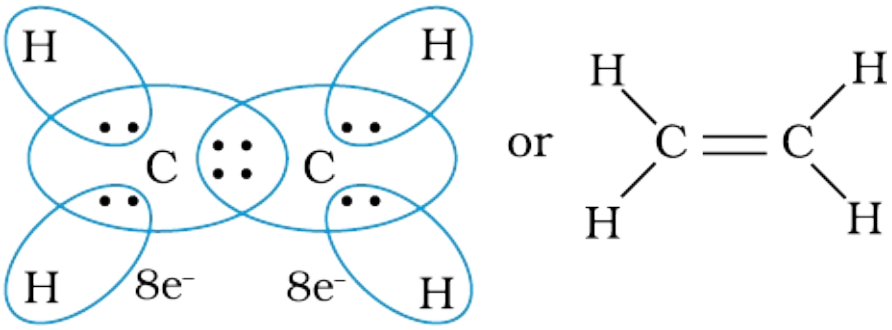
Each of the four Cl atoms along with the C atom attains octet of electrons

Thus, when two atoms share one electron pair they are said to be joined by a single covalent bond. In many compounds we have **multiple bonds** between atoms. The formation of multiple bonds envisages sharing of more than one electron pair between two atoms. **If two atoms share two pairs of electrons, the covalent bond between them is called a double bond.** For example, in the carbon dioxide molecule, we have two double bonds between the carbon and oxygen atoms. Similarly in ethene molecule the two carbon atoms are joined by a double bond.

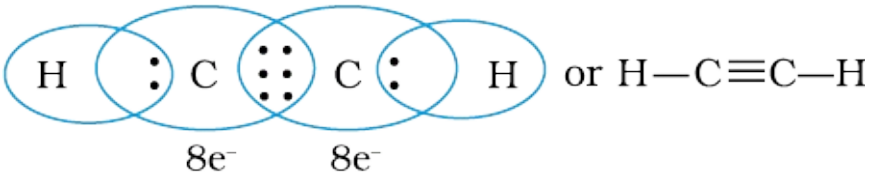
When combining atoms share three electron pairs as in the case of two nitrogen atoms in the N_2 molecule and the two carbon atoms in the ethyne molecule, a triple bond is formed.



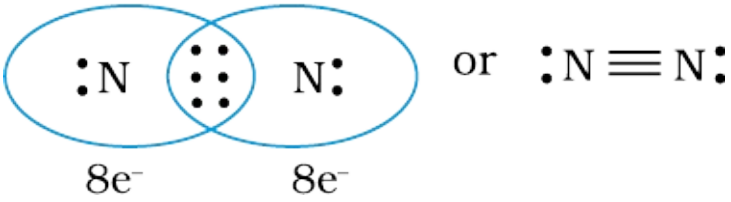
Double bonds in CO_2 molecule



C_2H_4 molecule



N_2 molecule



C_2H_2 molecule

4.1.3 Lewis Representation of Simple Molecules (the Lewis Structures)

The Lewis dot structures provide a picture of bonding in molecules and ions in terms of the shared pairs of electrons and the octet rule. While such a picture may not explain the bonding and behaviour of a molecule completely, it does help in understanding the formation and properties of a molecule to a large extent. Writing of Lewis dot structures of molecules is, therefore, very useful. The Lewis dot structures can be written by adopting the following steps:

- The total number of electrons required for writing the structures are obtained by adding the valence electrons of the combining atoms. For example, in the CH_4 molecule there are eight valence electrons available for bonding (4 from carbon and 4 from the four hydrogen

atoms).

• For anions, each negative charge would mean addition of one electron. For cations, each positive charge would result in subtraction of one electron from the total number of valence electrons. For example, for the CO_3^{2-} ion, the two negative charges indicate that there are two additional electrons than those provided by the neutral atoms. For NH_4^+ ion, one positive charge indicates the loss of one electron from the group of neutral atoms.

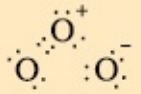
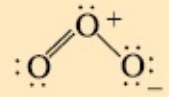
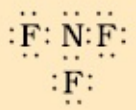
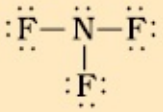
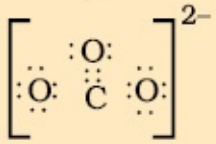
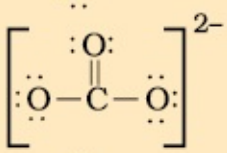
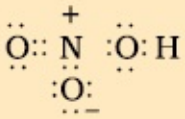
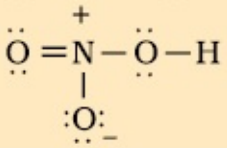
• Knowing the chemical symbols of the combining atoms and having knowledge of the skeletal structure of the compound (known or guessed intelligently), it is easy to distribute the total number of electrons as bonding shared pairs between the atoms in proportion to the total bonds.

• In general the least electronegative atom occupies the central position in the molecule/ion. For example in the NF_3 and CO_3^{2-}, nitrogen and carbon are the central atoms whereas fluorine and oxygen occupy the terminal positions.

• After accounting for the shared pairs of electrons for single bonds, the remaining electron pairs are either utilized for multiple bonding or remain as the lone pairs. The basic requirement being that each bonded atom gets an octet of electrons.

Lewis representations of a few molecules/ ions are given in Table 4.1.

Table 4.1 The Lewis Representation of Some Molecules

Molecule/Ion		Lewis Representation
H_2	H : H*	H – H
O_2	:Ö::Ö:	:Ö=Ö:
O_3		
NF_3		
CO_3^{2-}		
HNO_3		

** Each H atom attains the configuration of helium (a duplet of electrons)*

Problem 4.1

Write the Lewis dot structure of CO molecule.

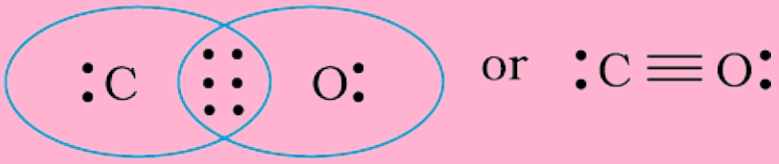
Solution

Step 1. Count the total number of valence electrons of carbon and oxygen atoms. The outer (valence) shell configurations of carbon and oxygen atoms are: $2s^2\ 2p^2$ and $2s^2\ 2p^4$, respectively. The valence electrons available are 4 + 6 =10.

Step 2. The skeletal structure of CO is written as: C O

Step 3. Draw a single bond (one shared electron pair) between C and O and complete the octet on O, the remaining two electrons are the lone pair on C.

This does not complete the octet on carbon and hence we have to resort to multiple bonding (in this case a triple bond) between C and O atoms. This satisfies the octet rule condition for both atoms.



Problem 4.2

Write the Lewis structure of the nitrite ion, NO_2^- .

Solution

Step 1. Count the total number of valence electrons of the nitrogen atom, the oxygen atoms and the additional one negative charge (equal to one electron).

N($2s^2\ 2p^3$), O ($2s^2\ 2p^4$)

5 + (2 × 6) +1 = 18 electrons

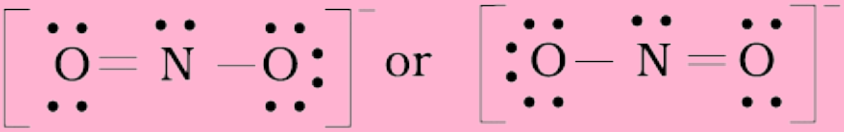
Step 2. The skeletal structure of NO_2^- is written as : O N O

Step 3. Draw a single bond (one shared electron pair) between the nitrogen and each of the oxygen atoms completing the octets on oxygen atoms. This, however, does not complete the octet on nitrogen if the remaining two electrons constitute lone pair on it.

Hence we have to resort to multiple bonding between nitrogen and one of the oxygen atoms (in this case a double bond). This leads to the following Lewis dot structures.



or



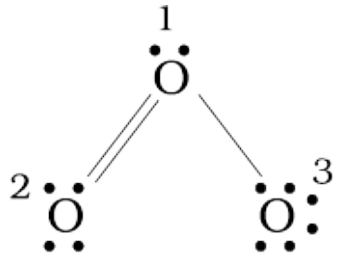
4.1.4 Formal Charge

Lewis dot structures, in general, do not represent the actual shapes of the molecules. In case of polyatomic ions, the net charge is possessed by the ion as a whole and not by a particular atom. It is, however, feasible to assign a formal charge on each atom. The formal charge of an atom in a polyatomic molecule or ion may be defined as the difference between the number of valence electrons of that atom in an isolated or free state and the number of electrons assigned to that atom in the Lewis structure. It is expressed as :

Formal charge (F.C.) on an atom in a Lewis structure = [total number of valence electrons in the free atom] − [total number of non bonding (lone pair) electrons] − (1/2) [total number of bonding(shared) electrons]

The counting is based on the assumption that the atom in the molecule owns one electron of each shared pair and both the electrons of a lone pair.

Let us consider the ozone molecule (O_3). The Lewis structure of O_3 may be drawn as :



The atoms have been numbered as 1, 2 and 3. The formal charge on:

- The central O atom marked 1

  $= 6 - 2 - \frac{1}{2}(6) = +1$

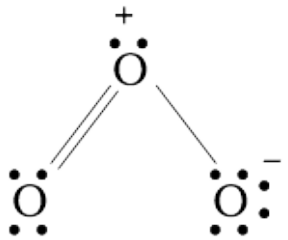
- The end O atom marked 2

  $= 6 - 4 - \frac{1}{2}(4) = 0$

- The end O atom marked 3

  $= 6 - 6 - \frac{1}{2}(2) = -1$

Hence, we represent O_3 along with the formal charges as follows:



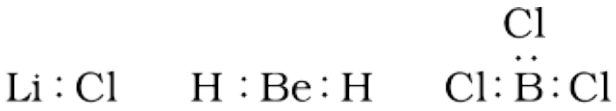
We must understand that formal charges do not indicate real charge separation within the molecule. Indicating the charges on the atoms in the Lewis structure only helps in keeping track of the valence electrons in the molecule. Formal charges help in the selection of the lowest energy structure from a number of possible Lewis structures for a given species. **Generally the lowest energy structure is the one with the smallest formal charges on the atoms. The formal charge is a factor based on a pure covalent view of bonding in which electron pairs are shared equally by neighbouring atoms.**

4.1.5 Limitations of the Octet Rule

The octet rule, though useful, is not universal. It is quite useful for understanding the structures of most of the organic compounds and it applies mainly to the second period elements of the periodic table. There are three types of exceptions to the octet rule.

The incomplete octet of the central atom

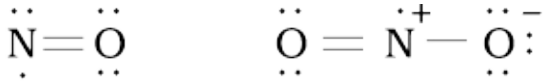
In some compounds, the number of electrons surrounding the central atom is less than eight. This is especially the case with elements having less than four valence electrons. Examples are LiCl, BeH_2 and BCl_3.



Li, Be and B have 1,2 and 3 valence electrons only. Some other such compounds are $AlCl_3$ and BF_3.

Odd-electron molecules

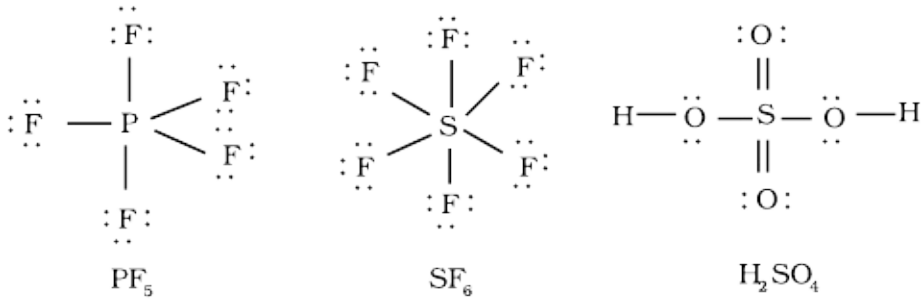
In molecules with an odd number of electrons like nitric oxide, NO and nitrogen dioxide, NO_2, the octet rule is not satisfied for all the atoms



The expanded octet

Elements in and beyond the third period of the periodic table have, apart from 3s and 3p orbitals, 3d orbitals also available for bonding. In a number of compounds of these elements there are more than eight valence electrons around the central atom. This is termed as the expanded octet. Obviously the octet rule does not apply in such cases.

Some of the examples of such compounds are: PF_5, SF_6, H_2SO_4 and a number of coordination compounds.

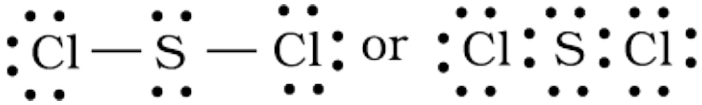


PF_5 — 10 electrons around the P atom

SF_6 — 12 electrons around the S atom

H_2SO_4 — 12 electrons around the S atom

Interestingly, sulphur also forms many compounds in which the octet rule is obeyed. In sulphur dichloride, the S atom has an octet of electrons around it.



Other drawbacks of the octet theory

- It is clear that octet rule is based upon the chemical inertness of noble gases. However, some noble gases (for example xenon and krypton) also combine with oxygen and fluorine to form a number of compounds like XeF_2, KrF_2, $XeOF_2$ etc.,
- This theory does not account for the shape of molecules.
- It does not explain the relative stability of the molecules being totally silent about the energy of a molecule.

4.2 Ionic or Electrovalent Bond

From the Kössel and Lewis treatment of the formation of an ionic bond, it follows that the formation of ionic compounds would primarily depend upon:

- The ease of formation of the positive and negative ions from the respective neutral atoms;
- The arrangement of the positive and negative ions in the solid, that is, the lattice of the crystalline compound.

The formation of a positive ion involves ionization, i.e., removal of electron(s) from the neutral atom and that of the negative ion involves the addition of electron(s) to the neutral atom.

$M(g) \rightarrow M^+(g) + e^-$;

Ionization enthalpy

$X(g) + e^- \rightarrow X^-(g)$;

Electron gain enthalpy

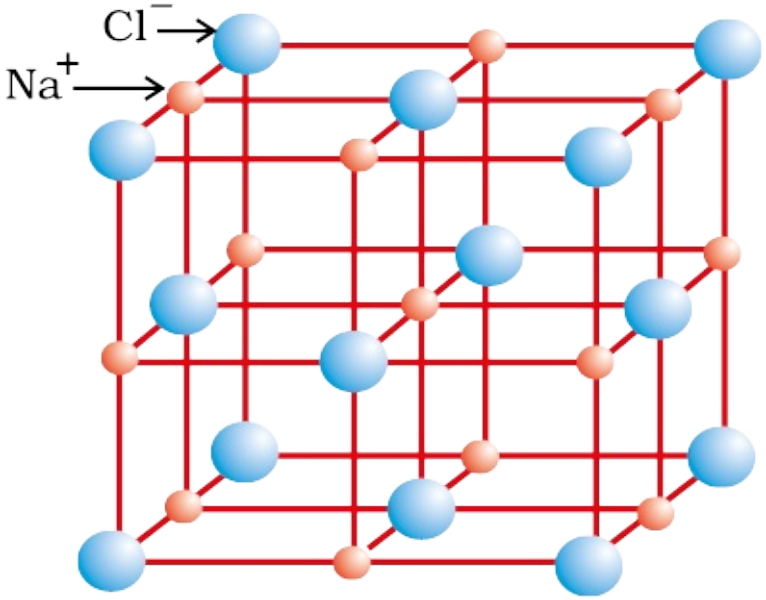
$M^+(g) + X^-(g) \rightarrow MX(s)$

The **electron gain enthalpy,** Δ_{eg}**H,** is the enthalpy change (Unit 3), when a gas phase atom in its ground state gains an electron. The electron gain process may be exothermic or endothermic. The ionization, on the other hand, is always endothermic. Electron affinity, is the negative of the energy change accompanying electron gain.

Obviously ionic bonds will be formed more easily between elements with comparatively low ionization enthalpies and elements with comparatively high negative value of electron gain enthalpy.

Most ionic compounds have cations derived from metallic elements and anions from non-metallic elements. The ammonium ion, NH_4^+ (made up of two non-metallic elements) is an exception. It forms the cation of a number of ionic compounds.

Ionic compounds in the crystalline state consist of orderly three-dimensional arrangements of cations and anions held together by coulombic interaction energies. These compounds crystallise in different crystal structures determined by the size of the ions, their packing arrangements and other factors. The crystal structure of sodium chloride, NaCl (rock salt), for example is shown below.



Rock salt structure

In ionic solids, the sum of the electron gain enthalpy and the ionization enthalpy may be positive but still the crystal structure gets stabilized due to the energy released in the formation of the crystal lattice. For example: the ionization enthalpy for $Na^+(g)$ formation from Na(g) is 495.8 kJ mol^{-1} ; while the electron gain enthalpy for the change $Cl(g) + e^- \rightarrow Cl^-(g)$ is, –348.7 kJ mol^{-1} only. The sum of the two, 147.1 kJ mol^{-1} is more than compensated for by the enthalpy of lattice formation of NaCl(s) (–788 kJ mol^{-1}). Therefore, the energy released in the processes is more than the energy absorbed. **Thus a qualitative measure of the stability of an ionic compound is provided by its enthalpy of lattice formation and not simply by achieving octet of electrons around the ionic species in gaseous state.**

Since lattice enthalpy plays a key role in the formation of ionic compounds, it is important that we learn more about it.

4.2.1 Lattice Enthalpy

The Lattice Enthalpy of an ionic solid is defined as the energy required to completely separate one mole of a solid ionic compound into gaseous constituent ions. For example, the lattice enthalpy of NaCl is 788 kJ mol^{-1}. This means that 788 kJ of energy is required to separate one mole of solid NaCl into one mole of Na^+ (g) and one mole of Cl^- (g) to an infinite distance.

This process involves both the attractive forces between ions of opposite charges and the repulsive forces between ions of like charge. The solid crystal being three-dimensional; it is not possible to calculate lattice enthalpy directly from the interaction of forces of attraction and repulsion only. Factors associated with the crystal geometry have to be included.

4.3 Bond Parameters

4.3.1 Bond Length

Bond length is defined as the equilibrium distance between the nuclei of two bonded atoms in a molecule. Bond lengths are measured by spectroscopic, X-ray diffraction and electron-diffraction techniques about which you will learn in higher classes. Each atom of the bonded pair contributes to the bond length (Fig. 4.1). In the case of a covalent bond, the contribution from each atom is called the covalent radius of that atom. **The covalent radius is measured approximately as the radius of an atom's core which is in contact with the core of an adjacent atom in a bonded situation.** The covalent radius is half of the distance between two similar atoms joined by a covalent bond in the same molecule. **The van der Waals radius represents the overall size of the atom which includes its valence shell in a nonbonded situation.** Further, the van der Waals radius is half of the distance between two similar atoms in

separate molecules in a solid. Covalent and van der Waals radii of chlorine are depicted in Fig.4.2

Some typical average bond lengths for single, double and triple bonds are shown in Table 4.2. Bond lengths for some common molecules are given in Table 4.3.

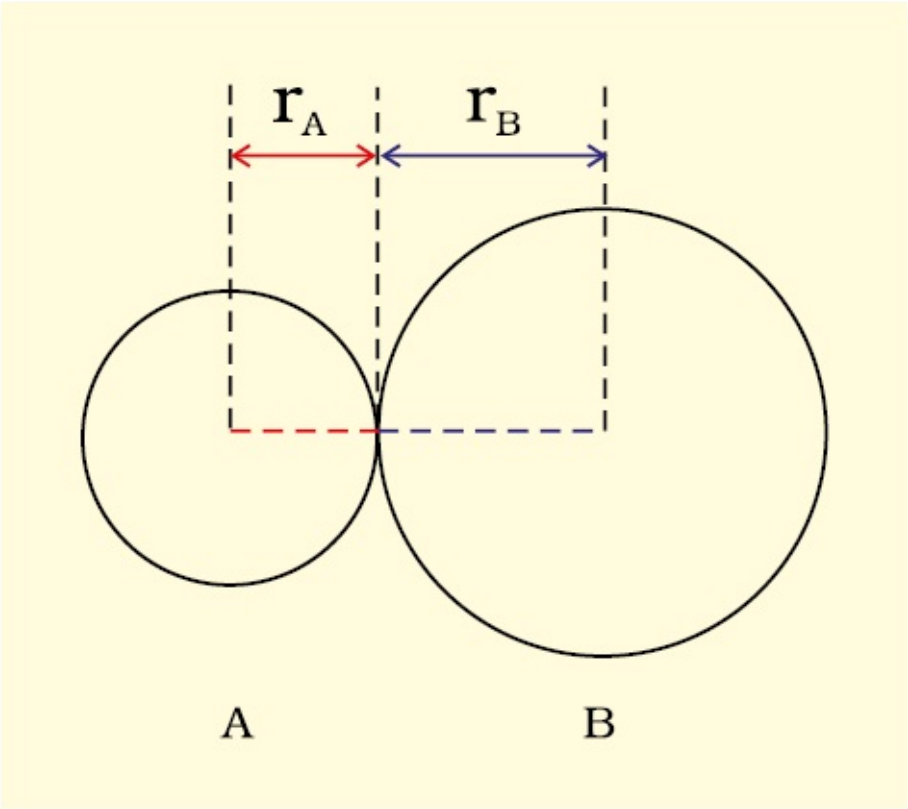


Fig. 4.1 The bond length in a covalent molecule AB.

$R = r_A + r_B$ (R is the bond length and r_A and r_B are the covalent radii of atoms A and B respectively)

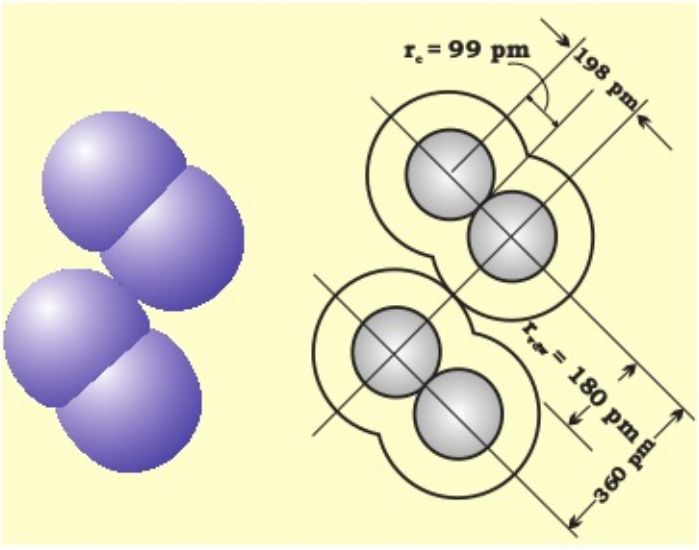
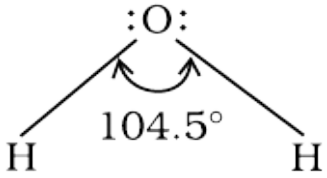


Fig. 4.2 Covalent and van der Waals radii in a chlorine molecule. The inner circles correspond to the size of the chlorine atom (r_{vdW} and r_c are van der Waals and covalent radii respectively).

The covalent radii of some common elements are listed in Table 4.4.

4.3.2 Bond Angle

It is defined as the angle between the orbitals containing bonding electron pairs around the central atom in a molecule/complex ion. Bond angle is expressed in degree which can be experimentally determined by spectroscopic methods. It gives some idea regarding the distribution of orbitals around the central atom in a molecule/complex ion and hence it helps us in determining its shape. For example H–O–H bond angle in water can be represented as under :



4.3.3 Bond Enthalpy

It is defined as the amount of energy required to break one mole of bonds of a particular type between two atoms in a gaseous state. The unit of bond enthalpy is kJ mol^{-1}. For example, the H – H bond enthalpy in hydrogen molecule is 435.8 kJ mol^{-1}.

$H_2(g) \rightarrow H(g) + H(g)$; $\Delta_a HV = 435.8$ kJ mol^{-1}

Similarly the bond enthalpy for molecules containing multiple bonds, for example O_2 and N_2 will be as under :

O_2 (O = O) (g) $\rightarrow$ O(g) + O(g); $\Delta_a HV = 498$ kJ mol^{-1}

N_2 (N ≡ N) (g) $\rightarrow$ N(g) + N(g); $\Delta_a HV = 946.0$ kJ mol^{-1}

It is important that larger the bond dissociation enthalpy, stronger will be the bond in the molecule. For a heteronuclear diatomic molecules like HCl, we have

HCl (g) $\rightarrow$ H(g) + Cl (g); $\Delta_a HV = 431.0$ kJ mol^{-1}

In case of polyatomic molecules, the measurement of bond strength is more complicated. For example in case of H_2O molecule, the enthalpy needed to break the two O – H bonds is not the same.

Table 4.2 Average Bond Lengths for Some Single, Double and Triple Bonds

Bond Type	Covalent Bond Length (pm)
O–H	96
C–H	107
N–O	136
C–O	143
C–N	143
C–C	154
C=O	121
N=O	122
C=C	133
C=N	138
C≡N	116
C≡C	120

Table 4.3 Bond Lengths in Some Common Molecules

Molecule	Bond Length (pm)
H_2 (H – H)	74
F_2 (F – F)	144
Cl_2 (Cl – Cl)	199
Br_2 (Br – Br)	228
I_2 (I – I)	267
N_2 (N ≡ N)	109
O_2 (O = O)	121
HF (H – F)	92
HCl (H – Cl)	127
HBr (H – Br)	141
HI (H – I)	160

Table 4.4 Covalent Radii, *rcov/(pm)

H	37						
C	77(1)	N	74 (1)	O	66(1)	F	64
	67 (2)		65(2)		57 (2)	Cl	99
	60(3)		55(3)				
		P	110	S	104(1)	Br	114
					95(2)		
		As	121	Se	104	I	133
		Sb	141	Te	137		

** The values cited are for single bonds, except where otherwise indicated in parenthesis. (See also Unit 3 for periodic trends).*

$H_2O(g) \rightarrow H(g) + OH(g)$; $\Delta_a H_1 V = 502$ kJ mol^{-1}

$OH(g) \rightarrow H(g) + O(g)$; $\Delta_a H_2 V = 427$ kJ mol^{-1}

The difference in the $\Delta_a HV$ value shows that the second O – H bond undergoes some change because of changed chemical environment. This is the reason for some difference in energy of the same O – H bond in different molecules like C_2H_5OH (ethanol) and water. Therefore in polyatomic molecules the term **mean or average bond enthalpy** is

used. It is obtained by dividing total bond dissociation enthalpy by the number of bonds broken as explained below in case of water molecule,

Average bond enthalpy = $\frac{502 + 427}{2}$

= 464.5 kJ mol^{-1}

4.3.4 Bond Order

In the Lewis description of covalent bond, the Bond Order is given by the number of bonds between the two atoms in a molecule. The bond order, for example in H_2 (with a single shared electron pair), in O_2 (with two shared electron pairs) and in N_2 (with three shared electron pairs) is 1,2,3 respectively. Similarly in CO (three shared electron pairs between C and O) the bond order is 3. For N_2, bond order is 3 and its $\Delta_a H^\ominus$ is 946 kJ mol^{-1}; being one of the highest for a diatomic molecule.

Isoelectronic molecules and ions have identical bond orders; for example, F_2 and O_2^{2-} have bond order 1. N_2, CO and NO^+ have bond order 3.

A general correlation useful for understanding the stablities of molecules is that: with increase in bond order, bond enthalpy increases and bond length decreases.

4.3.5 Resonance Structures

It is often observed that a single Lewis structure is inadequate for the representation of a molecule in conformity with its experimentally determined parameters. For example, the ozone, O_3 molecule can be equally represented by the structures I and II shown below:

In both structures we have a O–O single bond and a O=O double bond. The normal O–O and O=O bond lengths are 148 pm and 121 pm respectively. Experimentally determined oxygen-oxygen bond lengths in the O_3 molecule are same (128 pm). Thus the oxygen-oxygen bonds in

the O_3 molecule are intermediate between a double and a single bond. Obviously, this cannot be represented by either of the two Lewis structures shown above.

The concept of resonance was introduced to deal with the type of difficulty experienced in the depiction of accurate structures of molecules like O_3. **According to the concept of resonance, whenever a single Lewis structure cannot describe a molecule accurately, a number of structures with similar energy, positions of nuclei, bonding and non-bonding pairs of electrons are taken as the canonical structures of the hybrid which describes the molecule accurately.** Thus for O_3, the two structures shown above constitute the canonical structures or resonance structures and their hybrid i.e., the III structure represents the structure of O_3 more accurately. This is also called **resonance hybrid**. Resonance is represented by a double headed arrow.

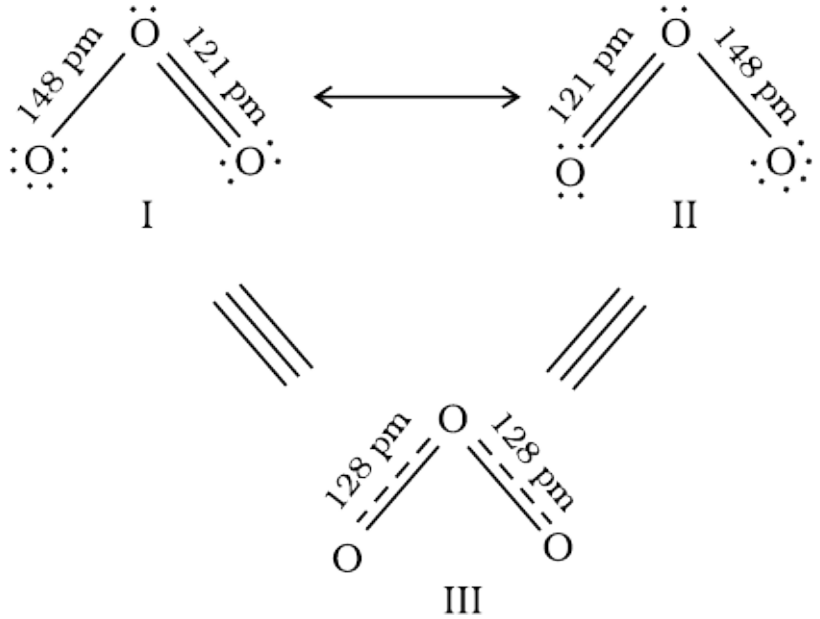


Fig. 4.3 Resonance in the O_3 molecule (structures I and II represent the two canonical forms while the structure III is the resonance hybrid)

Some of the other examples of resonance structures are provided by the

carbonate ion and the carbon dioxide molecule.

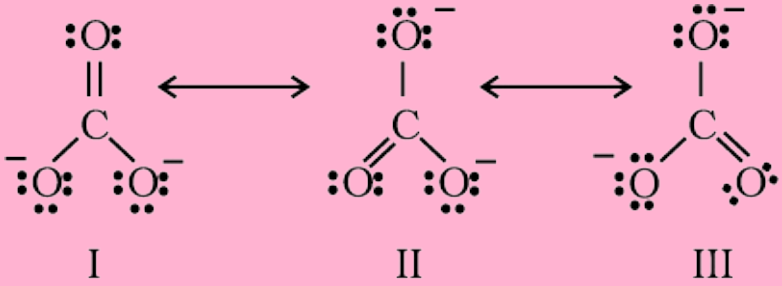
Problem 4.3

Explain the structure of CO_3^{2-} ion in terms of resonance.

Solution

The single Lewis structure based on the presence of two single bonds and one double bond between carbon and oxygen atoms is inadequate to represent the molecule accurately as it represents unequal bonds. According to the experimental findings, all carbon to oxygen bonds in CO_3^{2-} are equivalent. Therefore the carbonate ion is best described as a resonance hybrid of the canonical forms I, II, and III shown below.

Fig.4.4 Resonance in $CO_32–$, I, II and III represent the three canonical forms.

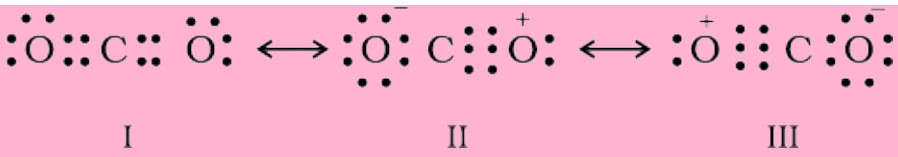


Problem 4.4

Explain the structure of CO_2 molecule.

Solution

The experimentally determined carbon to oxygen bond length in CO_2 is 115 pm. The lengths of a normal carbon to oxygen double bond (C=O) and carbon to oxygen triple bond (C≡O) are 121 pm and 110 pm respectively. The carbon-oxygen bond lengths in CO_2 (115 pm) lie between the values for C=O and C≡O. Obviously, a single Lewis structure cannot depict this position and it becomes necessary to write more than one Lewis structures and to consider that the structure of CO_2 is best described as a hybrid of the canonical or resonance forms I, II and III.



I II III

Fig. 4.5 Resonance in CO_2 molecule, I, II and III represent the three canonical forms.

In general, it may be stated that

- Resonance stabilizes the molecule as the energy of the resonance hybrid is less than the energy of any single cannonical structure; and,
- Resonance averages the bond characteristics as a whole.

Thus the energy of the O_3 resonance hybrid is lower than either of the two cannonical froms I and II (Fig 4.3).

Many **misconceptions** are associated with resonance and the same need to be dispelled. You should remember that :

- The cannonical forms have no real existence.
- The molecule does not exist for a certain fraction of time in one cannonical form and for other fractions of time in other cannonical forms.
- There is no such equilibrium between the cannonical forms as we have between tautomeric forms (keto and enol) in tautomerism.
- The molecule as such has a single structure which is the resonance hybrid of the cannonical forms and which cannot as such be depicted by a single Lewis structure.

4.3.6 Polarity of Bonds

The existence of a hundred percent ionic or covalent bond represents an ideal situation. In reality no bond or a compound is either completely covalent or ionic. Even in case of covalent bond between two hydrogen atoms, there is some ionic character.

When covalent bond is formed between two similar atoms, for example in

H_2, O_2, Cl_2, N_2 or F_2, the shared pair of electrons is equally attracted by the two atoms. As a result electron pair is situated exactly between the two identical nuclei. The bond so formed is called nonpolar covalent bond. Contrary to this in case of a heteronuclear molecule like HF, the shared electron pair between the two atoms gets displaced more towards fluorine since the electronegativity of fluorine (Unit 3) is far greater than that of hydrogen. The resultant covalent bond is a polar covalent bond.

As a result of polarisation, the molecule possesses the **dipole moment** (depicted below) which can be defined as the product of the magnitude of the charge and the distance between the centres of positive and negative charge. It is usually designated by a Greek letter 'μ'. Mathematically, it is expressed as follows :

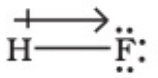
Dipole moment (μ) = charge (Q) × distaTable 4.2 Average Bond Lengths for Some Single, Double and Triple Bonds Bond Type Covalent Bond Lengthnce of separation (r)

Dipole moment is usually expressed in Debye units (D). The conversion factor is

$1\ D = 3.33564 \times 10^{-30}\ C\ m$

where C is coulomb and m is meter.

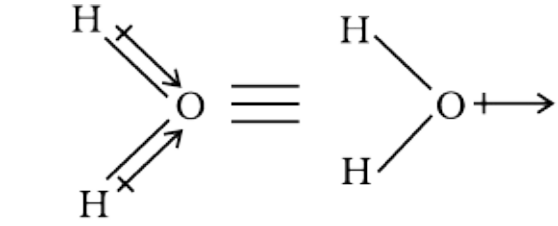
Further dipole moment is a vector quantity and by convention it is depicted by a small arrow with tail on the negative centre and head pointing towards the positive centre. But in chemistry presence of dipole moment is represented by the crossed arrow ($+\longrightarrow$) put on Lewis structure of the molecule. The cross is on positive end and arrow head is on negative end. For example the dipole moment of HF may be represented as :



This arrow symbolises the direction of the shift of electron density in the molecule. Note that the direction of crossed arrow is opposite to the

conventional direction of dipole moment vector.

In case of polyatomic molecules the dipole moment not only depend upon the individual dipole moments of bonds known as bond dipoles but also on the spatial arrangement of various bonds in the molecule. In such case, the dipole moment of a molecule is the vector sum of the dipole moments of various bonds. For example in H_2O molecule, which has a bent structure, the two O–H bonds are oriented at an angle of 104.5^0. Net dipole moment of 6.17×10^{-30} C m (1D = 3.33564×10^{-30} C m) is the resultant of the dipole moments of two O–H bonds.



(a) Bond dipole (b) Resultant dipole moment

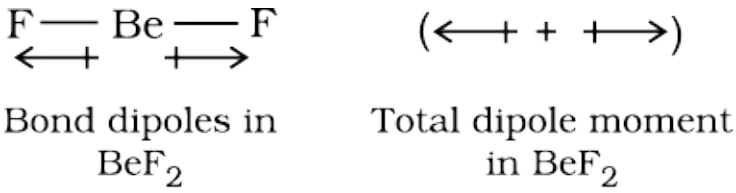


Peter Debye, the Dutch chemist received Nobel prize in 1936 for his work on X-ray diffraction and dipole moments. The magnitude of the dipole moment is given in Debye units in order to honour him.

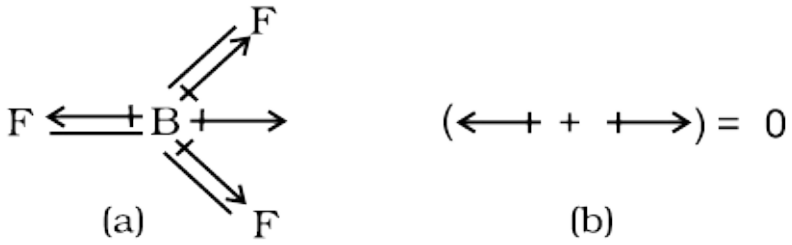
Net Dipole moment, μ = 1.85 D = $1.85 \times 3.33564 \times 10^{-30}$ C m = 6.17×10^{-30} C m

The dipole moment in case of BeF_2 is zero. This is because the two

equal bond dipoles point in opposite directions and cancel the effect of each other.

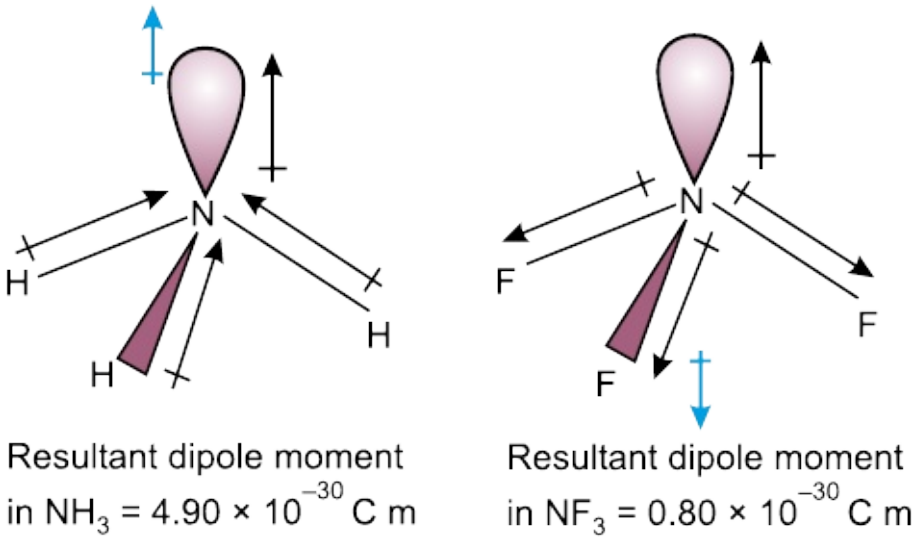


In tetra-atomic molecule, for example in BF_3, the dipole moment is zero although the B – F bonds are oriented at an angle of 120^o to one another, the three bond moments give a net sum of zero as the resultant of any two is equal and opposite to the third.



BF_3 molecule; representation of (a) bond dipoles and (b) total dipole moment

Let us study an interesting case of NH_3 and NF_3 molecule. Both the molecules have pyramidal shape with a lone pair of electrons on nitrogen atom. Although fluorine is more electronegative than nitrogen, the resultant dipole moment of NH_3 (4.90×10^{-30} C m) is greater than that of NF_3 (0.8×10^{-30} C m). This is because, in case of NH_3 the orbital dipole due to lone pair is in the same direction as the resultant dipole moment of the N – H bonds, whereas in NF_3 the orbital dipole is in the direction opposite to the resultant dipole moment of the three N–F bonds. The orbital dipole because of lone pair decreases the effect of the resultant N – F bond moments, which results in the low dipole moment of NF_3 as represented below :



Resultant dipole moment in $NH_3 = 4.90 \times 10^{-30}$ C m

Resultant dipole moment in $NF_3 = 0.80 \times 10^{-30}$ C m

Dipole moments of some molecules are shown in Table 4.5.

Just as all the covalent bonds have some partial ionic character, the ionic bonds also have partial covalent character. The partial covalent character of ionic bonds was discussed by Fajans in terms of the following rules:

- The smaller the size of the cation and the larger the size of the anion, the greater the covalent character of an ionic bond.
- The greater the charge on the cation, the greater the covalent character of the ionic bond.
- For cations of the same size and charge, the one, with electronic configuration

  $(n-1)d^n ns^o$, typical of transition metals, is more polarising than the one with a noble gas configuration, $ns^2\ np^6$, typical of alkali and alkaline earth metal cations.

  The cation polarises the anion, pulling the electronic charge toward itself and thereby increasing the electronic charge between the two. This is precisely what happens in a covalent bond, i.e., buildup of electron charge density between the nuclei. The polarising power of

the cation, the polarisability of the anion and the extent of distortion (polarisation) of anion are the factors, which determine the per cent covalent character of the ionic bond.

4.4 The Valence Shell Electron Pair Repulsion (VSEPR) Theory

As already explained, Lewis concept is unable to explain the shapes of molecules. This theory provides a simple procedure to predict the shapes of covalent molecules. Sidgwick and Powell in 1940, proposed a simple theory based on the repulsive interactions of the electron pairs in the valence shell of the atoms. It was further developed and redefined by Nyholm and Gillespie (1957).

Table 4.5 Dipole Moments of Selected Molecules

Type of Molecule	Example	Dipole Moment, μ(D)	Geometry
Molecule (AB)	HF	1.78	linear
	HCl	1.07	linear
	HBr	0.79	linear
	HI	0.38	linear
	H_2	0	linear
Molecule (AB_2)	H_2O	1.85	bent
	H_2S	0.95	bent
	CO_2	0	linear
Molecule (AB_3)	NH_3	1.47	trigonal-pyramidal
	NF_3	0.23	trigonal-pyramidal
	BF_3	0	trigonal-planar
Molecule (AB_4)	CH_4	0	tetrahedral
	$CHCl_3$	1.04	tetrahedral
	CCl_4	0	tetrahedral

The main postulates of VSEPR theory are as follows:

• The shape of a molecule depends upon the number of valence shell electron pairs (bonded or nonbonded) around the central atom.

• Pairs of electrons in the valence shell repel one another since their electron clouds are negatively charged.

• These pairs of electrons tend to occupy such positions in space that minimise repulsion and thus maximise distance between them.

• The valence shell is taken as a sphere with the electron pairs localising on the spherical surface at maximum distance from one another.
• A multiple bond is treated as if it is a single electron pair and the two or three electron pairs of a multiple bond are treated as a single super pair.
• Where two or more resonance structures can represent a molecule, the VSEPR model is applicable to any such structure.

The repulsive interaction of electron pairs decrease in the order:

Lone pair (lp) – Lone pair (lp) > Lone pair (lp) – Bond pair (bp) > Bond pair (bp) – Bond pair (bp)

Nyholm and Gillespie (1957) refined the VSEPR model by explaining the important difference between the lone pairs and bonding pairs of electrons. While the lone pairs are localised on the central atom, each bonded pair is shared between two atoms. As a result, the lone pair electrons in a molecule occupy more space as compared to the bonding pairs of electrons. This results in greater repulsion between lone pairs of electrons as compared to the lone pair - bond pair and bond pair - bond pair repulsions. These repulsion effects result in deviations from idealised shapes and alterations in bond angles in molecules.

For the prediction of geometrical shapes of molecules with the help of VSEPR theory, it is convenient to divide molecules into two categories as **(i) molecules in which the central atom has no lone pair and (ii) molecules in which the central atom has one or more lone pairs.**

Table 4.6 (page114) shows the arrangement of electron pairs about a central atom A (without any lone pairs) and geometries of some molecules/ions of the type AB. Table 4.7 (page 115) shows shapes of some simple molecules and ions in which the central atom has one or more lone pairs. Table 4.8 (page 116) explains the reasons for the distortions in the geometry of the molecule.

As depicted in Table 4.6, in the compounds of AB_2, AB_3, AB_4, AB_5 and

AB_6, the arrangement of electron pairs and the B atoms around the central atom A are : **linear, trigonal planar, tetrahedral, trigonal-bipyramidal and octahedral,** respectively. Such arrangement can be seen in the molecules like BF_3 (AB_3), CH_4 (AB_4) and PCl_5 (AB_5) as depicted below by their ball and stick models.

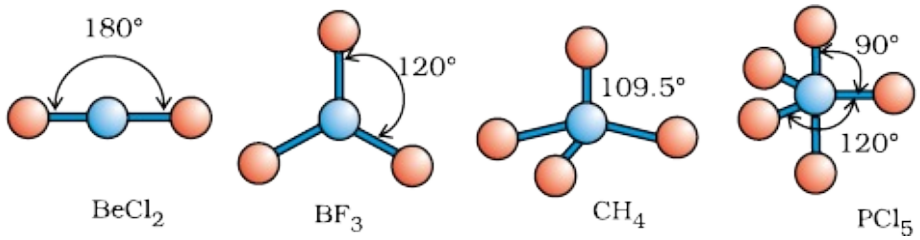


Fig. 4.6 The shapes of molecules in which central atom has no lone pair

The VSEPR Theory is able to predict geometry of a large number of molecules, especially the compounds of p-block elements accurately. It is also quite successful in determining the geometry quite-accurately even when the energy difference between possible structures is very small. The theoretical basis of the VSEPR theory regarding the effects of electron pair repulsions on molecular shapes is not clear and continues to be a subject of doubt and discussion.

Table 4.6 Geometry of Molecules in which the Central Atom has No Lone Pair of Electrons

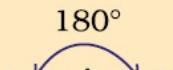
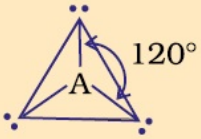
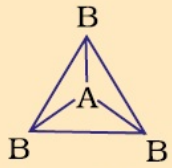
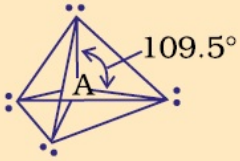
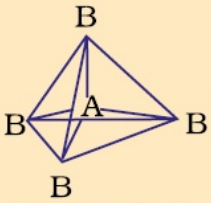
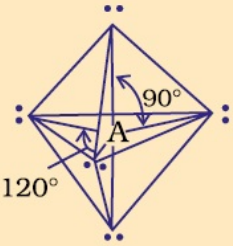
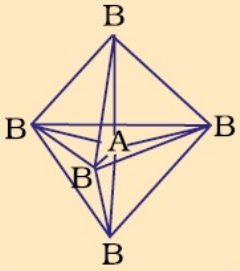
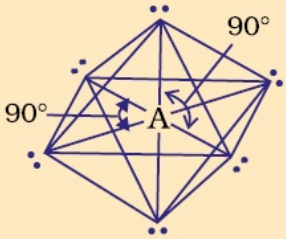
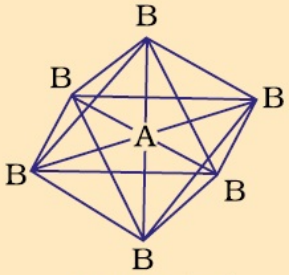
Number of electron pairs	Arrangement of electron pairs	Molecular geometry	Examples
2	 Linear	B—A—B Linear	$BeCl_2$, $HgCl_2$
3	 Trigonal planar	 Trigonal planar	BF_3
4	 Tetrahedral	 Tetrahedral	CH_4, NH_4^+
5	 Trigonal bipyramidal	 Trigonal bipyramidal	PCl_5
6	 Octahedral	 Octahedral	SF_6

Table 4.7 Shape (geometry) of Some Simple Molecules/Ions with Central Ions having One or More Lone Pairs of Electrons(E).

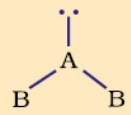
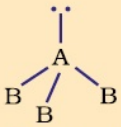
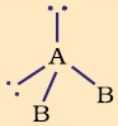
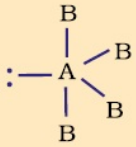
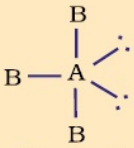
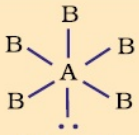
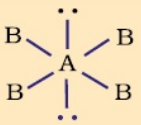
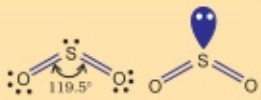
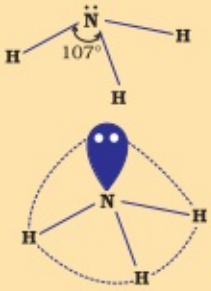
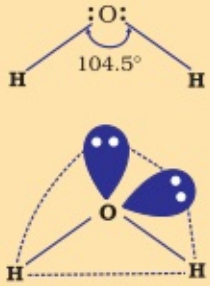
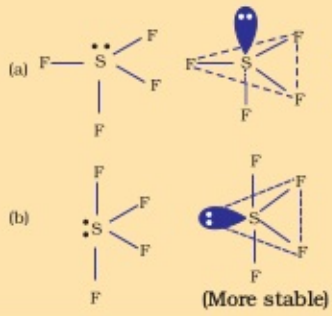
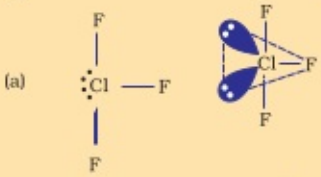
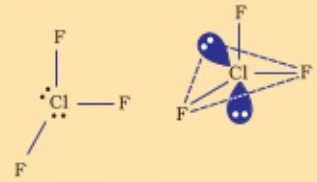
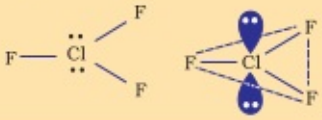
Molecule type	No. of bonding pairs	No. of lone pairs	Arrangement of electron pairs	Shape	Examples
AB_2E	2	1	 Trigonal planer	Bent	SO^2O_3
AB_3E	3	1	 Tetrahedral	Trigonal pyramidal	NH_3
AB_3E_2	2	2	 Tetrahedral	Bent	H_2O
AB_4E	4	1	 Trigonal bi-pyramidal	See saw	SF_4
AB_3E_2	3	2	 Trigonal bi-pyramidal	T-shape	ClF_3
AB_5E	5	1	 Octahedral	Square pyramid	BrF_5
AB_4E_2	4	2	 Octahedral	Square planer	XeF_4

Table 4.8 Shapes of Molecules containing Bond Pair and Lone Pair

Molecule type	No. of bonding pairs	No. of lone pairs	Arrangement of electrons	Shape	Reason for the shape acquired
AB_2E	4	1		Bent	Theoretically the shape should have been triangular planar but actually it is found to be bent or v-shaped. The reason being the lone pair-bond pair repulsion is much more as compared to the bond pair-bond pair repulsion. So the angle is reduced to 119.5° from 120°.
AB_3E	3	1		Trigonal pyramidal	Had there been a bp in place of lp the shape would have been tetrahedral but one lone pair is present and due to the repulsion between lp-bp (which is more than bp-bp repulsion) the angle between bond pairs is reduced to 107° from 109.5°.
AB_2E_2	2	2		Bent	The shape should have been tetrahedral if there were all bp but two lp are present so the shape is distorted tetrahedral or angular. The reason is lp-lp repulsion is more than lp-bp repulsion which is more than bp-bp repulsion. Thus, the angle is reduced to 104.5° from 109.5°.
AB_4E	4	1		See-saw	In (a) the lp is present at axial position so there are three lp—bp repulsions at 90°. In (b) the lp is in an equatorial position, and there are two lp—bp repulsions. Hence, arrangement (b) is more stable. The shape shown in (b) is described as a distorted tetrahedron, a folded square or a see-saw.

Molecule type	No. of bonding pairs	No. of lone pairs	Arrangement of electrons	Shape	Reason for the shape acquired
AB_3E_2	3	2	(a)  (b)  (c) 	T-shape	In (a) the lp are at equatorial position so there are less lp-bp repulsions as compared to others in which the lp are at axial positions. So structure (a) is most stable. (T-shaped).

4.5 Valence Bond Theory

As we know that Lewis approach helps in writing the structure of molecules but it fails to explain the formation of chemical bond. It also does not give any reason for the difference in bond dissociation enthalpies and bond lengths in molecules like H_2 (435.8 kJ mol^{-1}, 74 pm) and F_2 (155 kJ mol^{-1}, 144 pm), although in both the cases a single covalent bond is formed by the sharing of an electron pair between the respective atoms. It also gives no idea about the shapes of polyatomic molecules.

Similarly the VSEPR theory gives the geometry of simple molecules but theoretically, it does not explain them and also it has limited applications. To overcome these limitations the two important theories based on quantum mechanical principles are introduced. These are valence bond (VB) theory and molecular orbital (MO) theory.

Valence bond theory was introduced by Heitler and London (1927) and developed further by Pauling and others. A discussion of the valence bond theory is based on the knowledge of atomic orbitals, electronic

configurations of elements (Units 2), the overlap criteria of atomic orbitals, the hybridization of atomic orbitals and the principles of variation and superposition. A rigorous treatment of the VB theory in terms of these aspects is beyond the scope of this book. Therefore, for the sake of convenience, valence bond theory has been discussed in terms of qualitative and non-mathematical treatment only. To start with, let us consider the formation of hydrogen molecule which is the simplest of all molecules.

Consider two hydrogen atoms A and B approaching each other having nuclei N_A and N_B and electrons present in them are represented by e_A and e_B. When the two atoms are at large distance from each other, there is no interaction between them. As these two atoms approach each other, new attractive and repulsive forces begin to operate.

Attractive forces arise between:

(i) nucleus of one atom and its own electron that is $N_A – e_A$ and $N_B – e_B$.

(ii) nucleus of one atom and electron of other atom i.e., $N_A – e_B$, $N_B – e_A$.

Similarly repulsive forces arise between

(i) electrons of two atoms like $e_A – e_B$,

(ii) nuclei of two atoms $N_A – N_B$.

Attractive forces tend to bring the two atoms close to each other whereas repulsive forces tend to push them apart (Fig. 4.7).

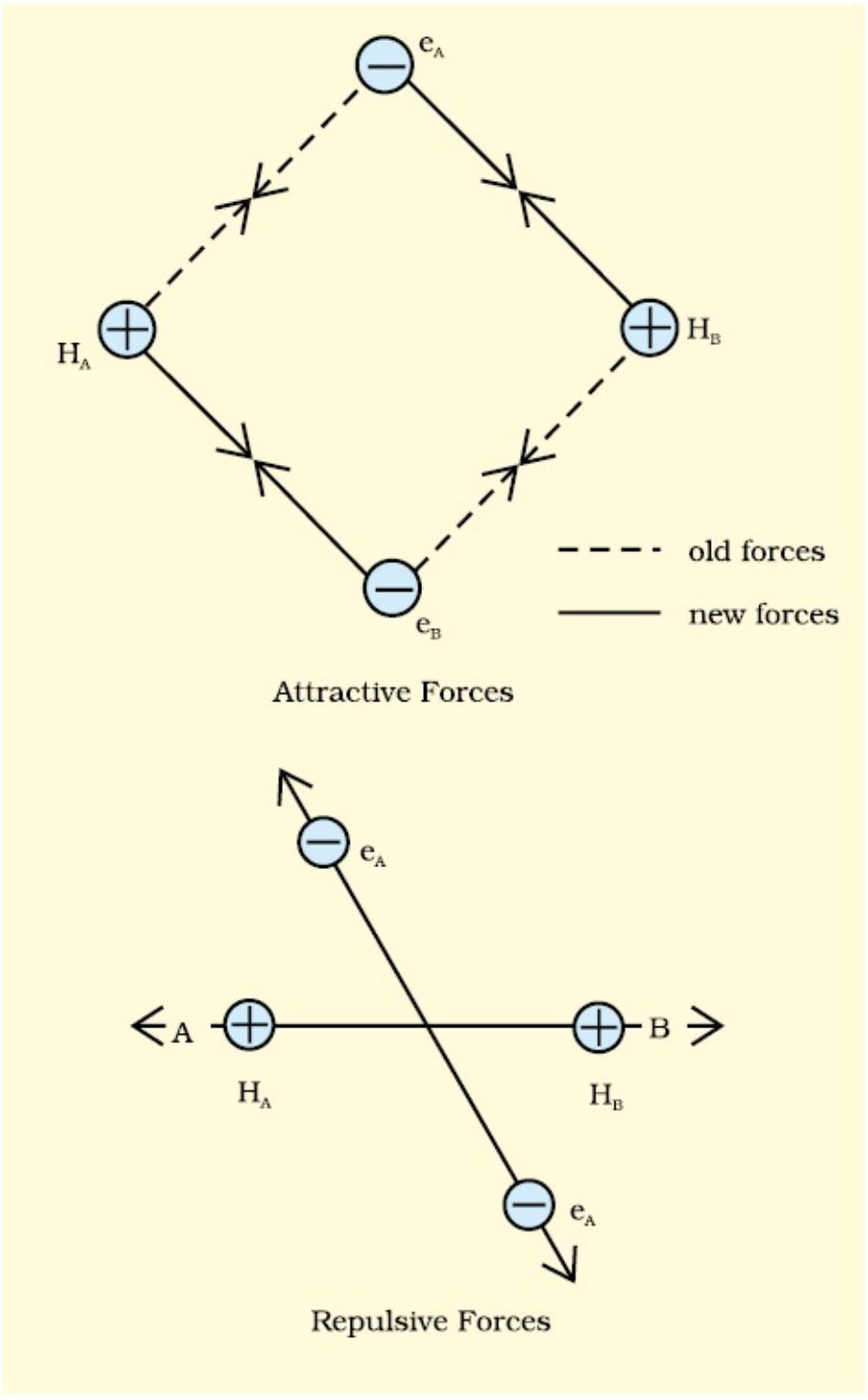


Fig. 4.7 Forces of attraction and repulsion during the formation of H_2 molecule.

Experimentally it has been found that the magnitude of new attractive force is more than the new repulsive forces. As a result, two atoms approach each other and potential energy decreases. Ultimately a stage

is reached where the net force of attraction balances the force of repulsion and system acquires minimum energy. At this stage two hydrogen atoms are said to be bonded together to form a stable molecule having the bond length of 74 pm.

Since the energy gets released when the bond is formed between two hydrogen atoms, the hydrogen molecule is more stable than that of isolated hydrogen atoms. The energy so released is called as **bond enthalpy**, which is corresponding to minimum in the curve depicted in Fig. 4.8. Conversely, 435.8 kJ of energy is required to dissociate one mole of H_2 molecule.

$$H_2(g) + 435.8 \text{ kJ mol}^{-1} \rightarrow H(g) + H(g)$$

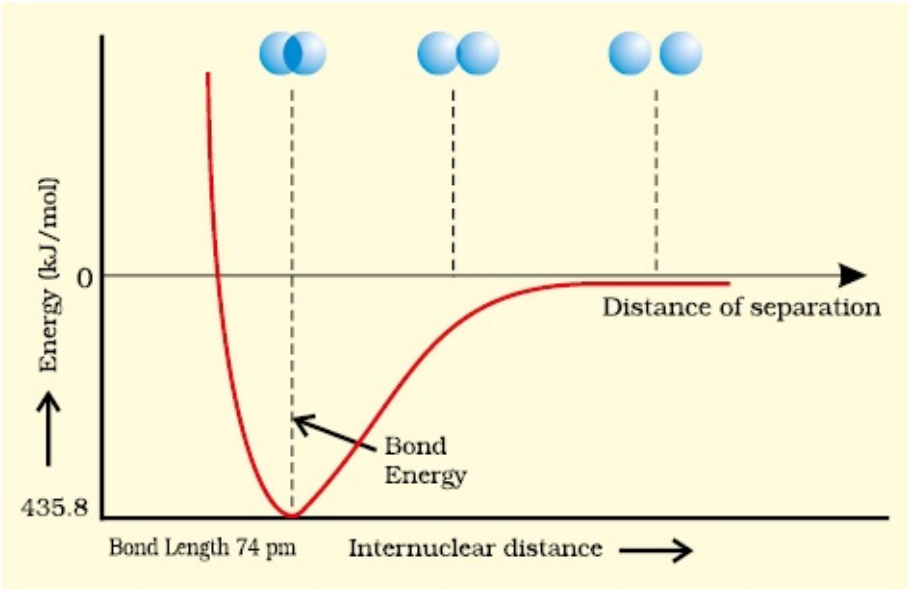


Fig. 4.8 The potential energy curve for the formation of H_2 molecule as a function of internuclear distance of the H atoms. The minimum in the curve corresponds to the most stable state of H_2.

4.5.1 Orbital Overlap Concept

In the formation of hydrogen molecule, there is a minimum energy state when two hydrogen atoms are so near that their atomic orbitals undergo partial interpenetration. This partial merging of atomic orbitals is called overlapping of atomic orbitals which results in the pairing of electrons.

The extent of overlap decides the strength of a covalent bond. In general, greater the overlap the stronger is the bond formed between two atoms. Therefore, according to orbital overlap concept, the formation of a covalent bond between two atoms results by pairing of electrons present in the valence shell having opposite spins.

4.5.2 Directional Properties of Bonds

As we have already seen, the covalent bond is formed by overlapping of atomic orbitals. The molecule of hydrogen is formed due to the overlap of 1s-orbitals of two H atoms.

In case of polyatomic molecules like CH_4, NH_3 and H_2O, the geometry of the molecules is also important in addition to the bond formation. For example why is it so that CH_4 molecule has tetrahedral shape and HCH bond angles are 109.5°? Why is the shape of NH_3 molecule pyramidal ?

The valence bond theory explains the shape, the formation and directional properties of bonds in polyatomic molecules like CH_4, NH_3 and H_2O, etc. in terms of overlap and hybridisation of atomic orbitals.

4.5.3 Overlapping of Atomic Orbitals

When orbitals of two atoms come close to form bond, their overlap may be positive, negative or zero depending upon the sign (phase) and direction of orientation of amplitude of orbital wave function in space (Fig. 4.9). Positive and negative sign on boundary surface diagrams in the Fig. 4.9 show the sign (phase) of orbital wave function and are not related to charge. Orbitals forming bond should have same sign (phase) and orientation in space. This is called positive overlap. Various overlaps of s and p orbitals are depicted in Fig. 4.9.

The criterion of overlap, as the main factor for the formation of covalent bonds applies uniformly to the homonuclear/heteronuclear diatomic

molecules and polyatomic molecules. We know that the shapes of CH_4, NH_3, and H_2O molecules are tetrahedral, pyramidal and bent respectively. It would be therefore interesting to use VB theory to find out if these geometrical shapes can be explained in terms of the orbital overlaps.

Let us first consider the CH_4 (methane) molecule. The electronic configuration of carbon in its ground state is [He]$2s^2$ $2p^2$ which in the excited state becomes [He] $2s^1$ $2p_x^1$ $2p_y^1$ $2p_z^1$. The energy required for this excitation is compensated by the release of energy due to overlap between the orbitals of carbon and the hydrogen.The four atomic orbitals of carbon, each with an unpaired electron can overlap with the 1s orbitals of the four H atoms which are also singly occupied. This will result in the formation of four C-H bonds. It will, however, be observed that while the three p orbitals of carbon are at 90° to one another, the HCH angle for these will also be 90°. That is three C-H bonds will be oriented at 90° to one another. The 2s orbital of carbon and the 1s orbital of H are spherically symmetrical and they can overlap in any direction. Therefore the direction of the fourth C-H bond cannot be ascertained. This description does not fit in with the tetrahedral HCH angles of 109.5°. Clearly, it follows that simple atomic orbital overlap does not account for the directional characteristics of bonds in CH_4. Using similar procedure and arguments, it can be seen that in the case of NH_3 and H_2O molecules, the HNH and HOH angles should be 90°. This is in disagreement with the actual bond angles of 107° and 104.5° in the NH_3 and H_2O molecules respectively.

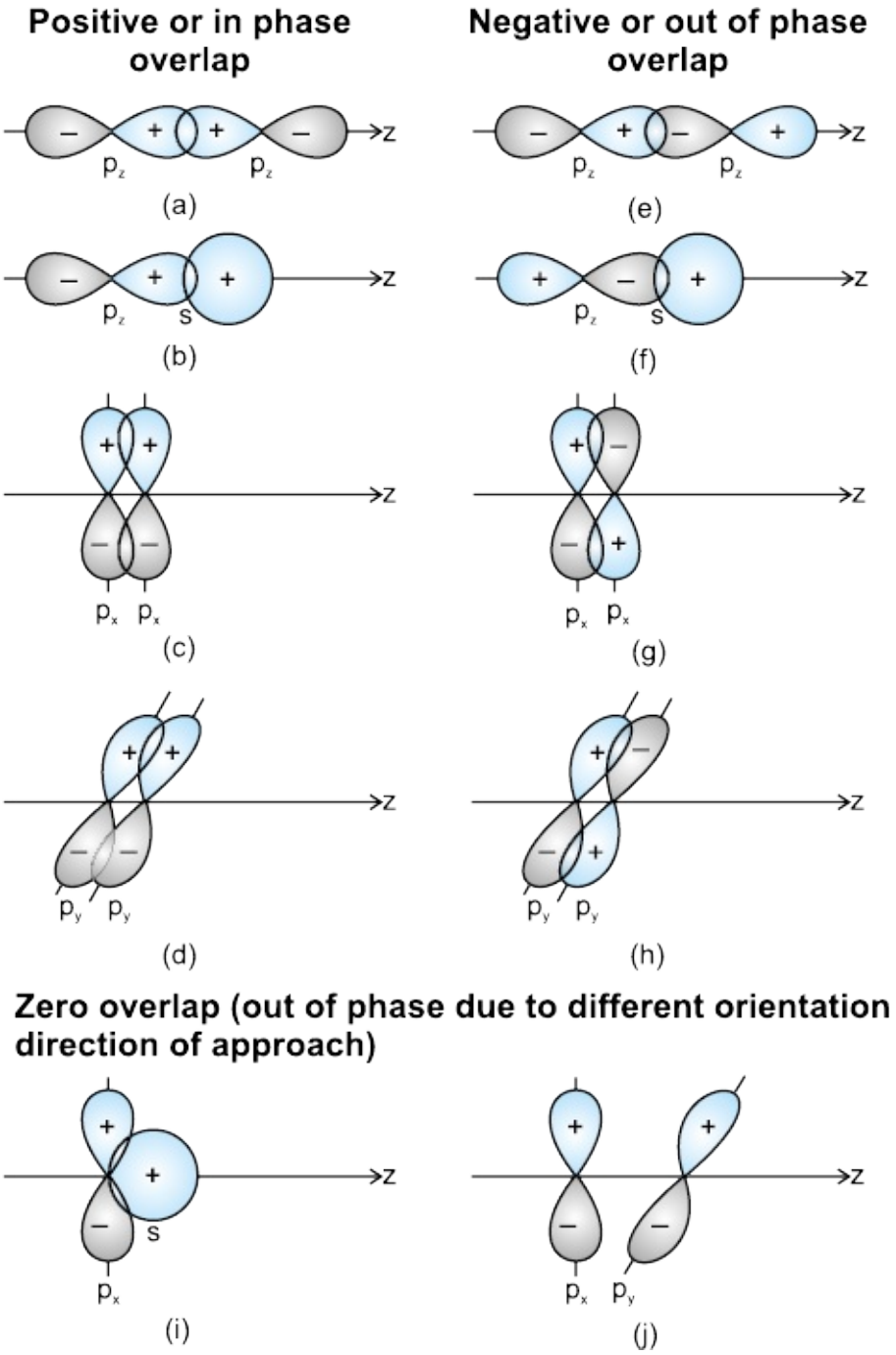


Fig.4.9 Positive, negative and zero overlaps of s and p atomic orbitals

4.5.4 Types of Overlapping and Nature of Covalent Bonds

The covalent bond may be classified into two types depending upon the types of overlapping:

(i) Sigma(σ) bond, and (ii) pi(π) bond

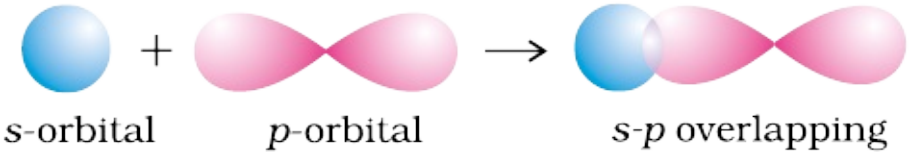
(i) Sigma(σ) bond : This type of covalent bond is formed by the end to end (head-on) overlap of bonding orbitals along the internuclear axis. This is called as head on overlap or axial overlap. This can be formed by any one of the following types of combinations of atomic orbitals.

• **s-s overlapping :** In this case, there is overlap of two half filled s-orbitals along the internuclear axis as shown below :

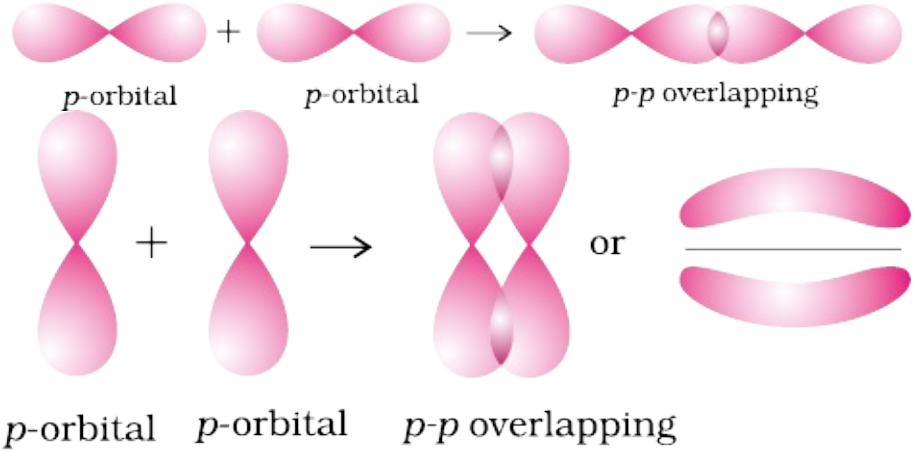
• **s-p overlapping:** This type of overlap occurs between half filled s-orbitals of one atom and half filled p-orbitals of another atom.



• **p–p overlapping :** This type of overlap takes place between half filled p-orbitals of the two approaching atoms.



(ii) **pi(π) bond :** In the formation of π bond the atomic orbitals overlap in such a way that their axes remain parallel to each other and perpendicular to the internuclear axis. The orbitals formed due to sidewise overlapping consists of two saucer type charged clouds above and below the plane of the participating atoms.



4.5.5 Strength of Sigma and pi Bonds

Basically the strength of a bond depends upon the extent of overlapping. In case of sigma bond, the overlapping of orbitals takes place to a larger extent. Hence, it is stronger as compared to the pi bond where the extent of overlapping occurs to a smaller extent. Further, it is important to note that in the formation of multiple bonds between two atoms of a molecule, pi bond(s) is formed in addition to a sigma bond.

4.6 Hybridisation

In order to explain the characteristic geometrical shapes of polyatomic molecules like CH_4, NH_3 and H_2O etc., Pauling introduced the concept of hybridisation. According to him the atomic orbitals combine to form new set of equivalent orbitals known as **hybrid orbitals**. Unlike pure orbitals, the hybrid orbitals are used in bond formation. The phenomenon is known as **hybridisation** which can be defined as the process of intermixing of the orbitals of slightly different energies so as to redistribute their energies, resulting in the formation of new set of orbitals of equivalent energies and shape. For example when one 2s and three 2p-orbitals of carbon hybridise, there is the formation of four new sp^3 hybrid orbitals.

Salient features of hybridisation: The main features of hybridisation are as under :

1. The number of hybrid orbitals is equal to the number of the atomic orbitals that get hybridised.
2. The hybridised orbitals are always equivalent in energy and shape.
3. The hybrid orbitals are more effective in forming stable bonds than the pure atomic orbitals.
4. These hybrid orbitals are directed in space in some preferred direction to have minimum repulsion between electron pairs and thus a stable arrangement. Therefore, the type of hybridisation indicates the geometry of the molecules.

Important conditions for hybridisation

(i) The orbitals present in the valence shell of the atom are hybridised.

(ii) The orbitals undergoing hybridisation should have almost equal energy.

(iii) Promotion of electron is not essential condition prior to hybridisation.

(iv) It is not necessary that only half filled orbitals participate in hybridisation. In some cases, even filled orbitals of valence shell take part in hybridisation.

4.6.1 Types of Hybridisation

There are various types of hybridisation involving s, p and d orbitals. The different types of hybridisation are as under:

(I) sp hybridisation: This type of hybridisation involves the mixing of one s and one p orbital resulting in the formation of two equivalent sp hybrid orbitals. The suitable orbitals for sp hybridisation are s and p_z, if the hybrid orbitals are to lie along the z-axis. Each sp hybrid orbitals has 50% s-character and 50% p-character. Such a molecule in which the central atom is sp-hybridised and linked directly to two other central atoms possesses linear geometry. This type of hybridisation is also known as diagonal hybridisation.

The two sp hybrids point in the opposite direction along the z-axis with projecting positive lobes and very small negative lobes, which provides more effective overlapping resulting in the formation of stronger bonds.

Example of molecule having sp hybridisation

$BeCl_2$: The ground state electronic configuration of Be is $1s^2 2s^2$. In the exited state one of the 2s-electrons is promoted to vacant 2p orbital to account for its bivalency. One 2s and one 2p-orbital gets hybridised to form two sp hybridised orbitals. These two sp hybrid orbitals are oriented in opposite direction forming an angle of 180°. Each of

the sp hybridised orbital overlaps with the 2p-orbital of chlorine axially and form two Be-Cl sigma bonds. This is shown in Fig. 4.10.

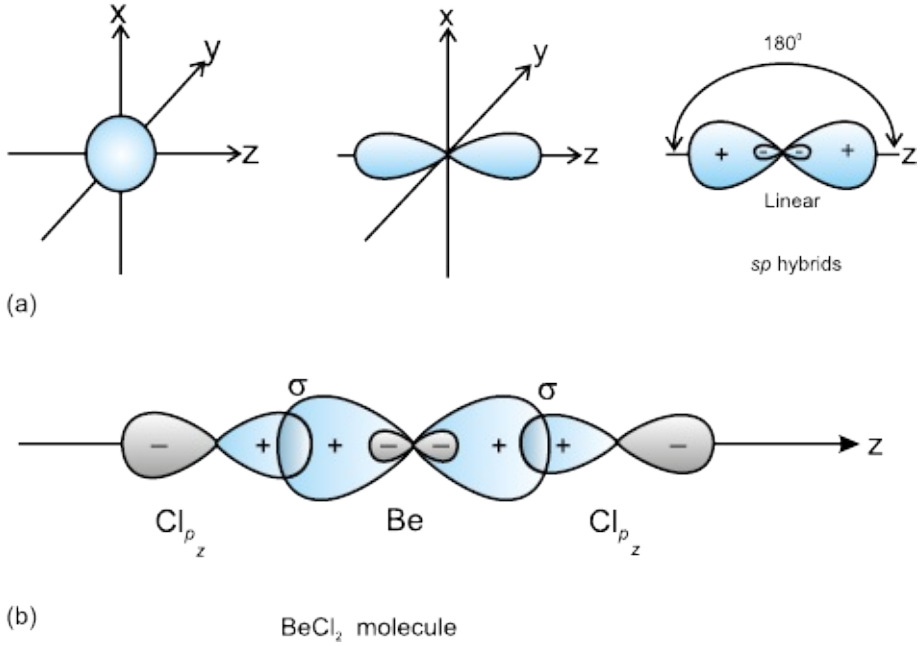


Fig.4.10 (a) Formation of sp hybrids from s and p orbitals; (b) Formation of the linear BeCl2 molecule

(II) sp^2 hybridisation : In this hybridisation there is involvement of one s and two

p-orbitals in order to form three equivalent sp^2 hybridised orbitals. For example, in BCl_3 molecule, the ground state electronic configuration of central boron atom is $1s^2 2s^2 2p^1$. In the excited state, one of the 2s electrons is promoted to vacant 2p orbital as a result boron has three unpaired electrons. These three orbitals (one 2s and two 2p) hybridise to form three sp^2 hybrid orbitals. The three hybrid orbitals so formed are oriented in a trigonal planar arrangement and overlap with 2p orbitals of chlorine to form three B-Cl bonds. Therefore, in BCl_3 (Fig. 4.11), the geometry is trigonal planar with ClBCl bond angle of 120°.

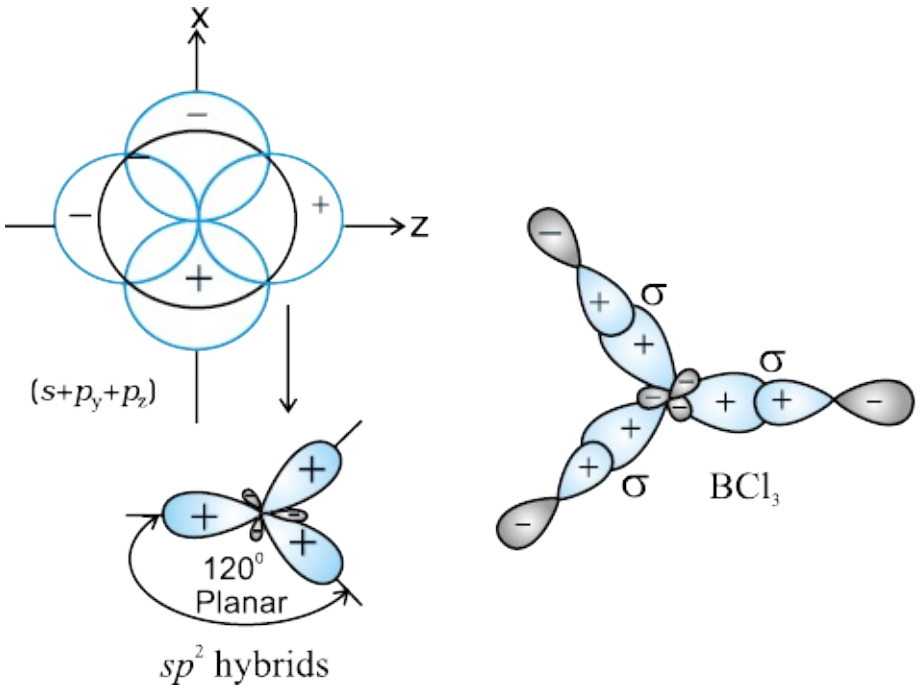


Fig.4.11 Formation of sp2 hybrids and the BCl_3 molecule

(III) sp^3 hybridisation: This type of hybridisation can be explained by taking the example of CH_4 molecule in which there is mixing of one s-orbital and three p-orbitals of the valence shell to form four sp^3 hybrid orbital of equivalent energies and shape. There is 25% s-character and 75% p-character in each sp^3 hybrid orbital. The four sp^3 hybrid orbitals so formed are directed towards the four corners of the tetrahedron. The angle between sp^3 hybrid orbital is 109.5° as shown in Fig. 4.12.

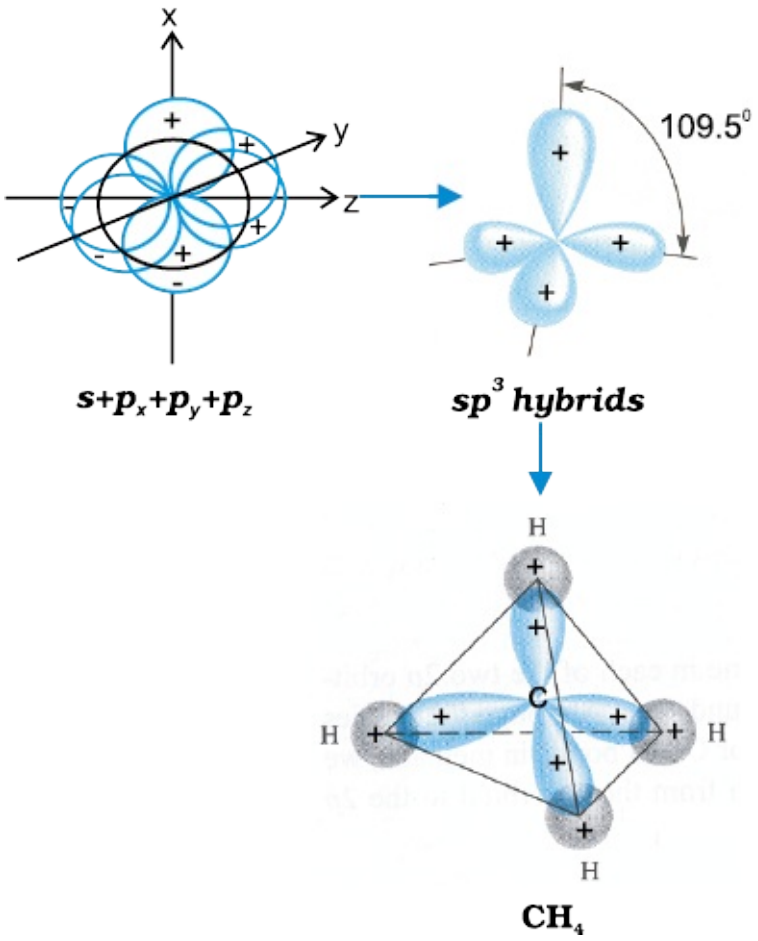


Fig.4.12 Formation of sp^3 hybrids by the combination of s , px , py and pz atomic orbitals of carbon and the formation of CH4 molecule

The structure of NH_3 and H_2O molecules can also be explained with the help of sp^3 hybridisation. In NH_3, the valence shell (outer) electronic configuration of nitrogen in the ground state is $2S^2 2p_x^1 2p_y^1 2p_z^1$ having three unpaired electrons in the sp^3 hybrid orbitals and a lone pair of electrons is present in the fourth one. These three hybrid orbitals overlap with 1s orbitals of hydrogen atoms to form three N–H sigma bonds. We know that the force of repulsion between a lone pair and a bond pair is more than the force of repulsion between two bond pairs of electrons. The molecule thus gets distorted and the bond angle is reduced to 107°

from 109.5°. The geometry of such a molecule will be pyramidal as shown in Fig. 4.13.

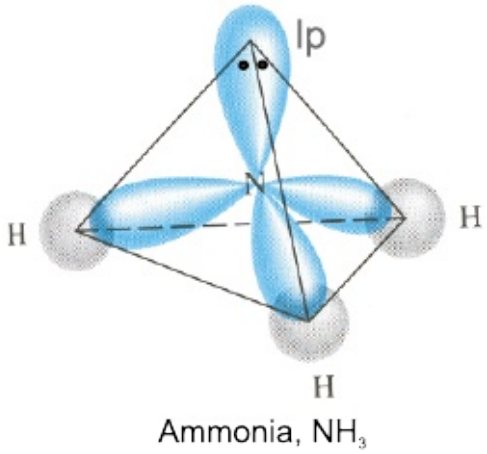


Fig.4.13 Formation of NH_3 molecule

In case of H_2O molecule, the four oxygen orbitals (one 2s and three 2p) undergo sp^3 hybridisation forming four sp^3 hybrid orbitals out of which two contain one electron each and the other two contain a pair of electrons. These four sp^3 hybrid orbitals acquire a tetrahedral geometry, with two corners occupied by hydrogen atoms while the other two by the lone pairs. The bond angle in this case is reduced to 104.5° from 109.5° (Fig. 4.14) and the molecule thus acquires a V-shape or angular geometry.

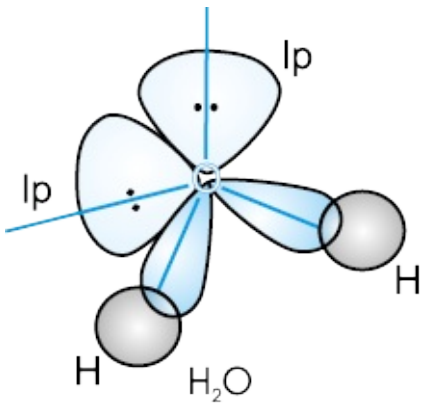


Fig.4.14 Formation of H2O molecule

4.6.2 Other Examples of sp^3, sp^2 and sp Hybridisation

sp^3 Hybridisation in C2H6 molecule: In ethane molecule both the carbon atoms assume sp^3 hybrid state. One of the four sp^3 hybrid orbitals of carbon atom overlaps axially with similar orbitals of other atom to form sp^3-sp^3 sigma bond while the other three hybrid orbitals of each carbon atom are used in forming sp^3–s sigma bonds with hydrogen atoms as discussed in section 4.6.1(iii). Therefore in ethane C–C bond length is 154 pm and each C–H bond length is 109 pm.

sp^2 Hybridisation in C_2H_4: In the formation of ethene molecule, one of the sp^2 hybrid orbitals of carbon atom overlaps axially with sp^2 hybridised orbital of another carbon atom to form C–C sigma bond. While the other two sp^2 hybrid orbitals of each carbon atom are used for making sp^2–s sigma bond with two hydrogen atoms. The unhybridised orbital (2px or 2py) of one carbon atom overlaps sidewise with the similar orbital of the other carbon atom to form weak π bond, which consists of two equal electron clouds distributed above and below the plane of carbon and hydrogen atoms.

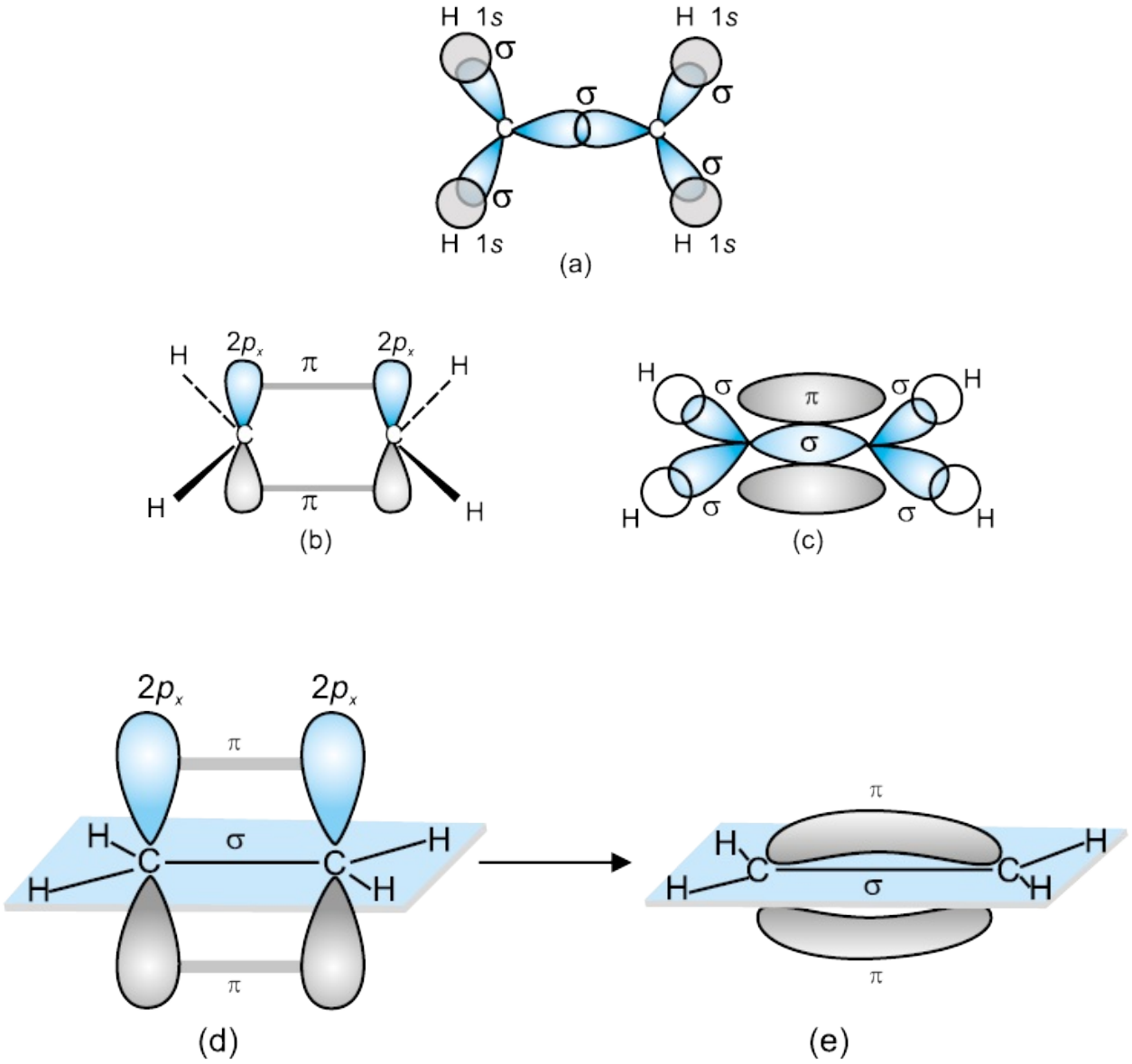


Fig. 4.15 Formation of sigma and pi bonds in ethene

Thus, in ethene molecule, the carbon-carbon bond consists of one sp^2–sp^2 sigma bond and one pi (π) bond between p orbitals which are not used in the hybridisation and are perpendicular to the plane of molecule; the bond length 134 pm. The C–H bond is sp^2–s sigma with bond length 108 pm. The H–C–H bond angle is 117.6° while the H–C–C angle is 121°. The formation of sigma and pi bonds in ethene is shown in Fig. 4.15.

sp Hybridisation in C_2H_2 : In the formation of ethyne molecule, both the carbon atoms undergo sp-hybridisation having two unhybridised orbital i.e., $2p_y$ and $2p_x$.

One sp hybrid orbital of one carbon atom overlaps axially with sp hybrid orbital of the other carbon atom to form C–C sigma bond, while the other hybridised orbital of each carbon atom overlaps axially with the half filled s orbital of hydrogen atoms forming σ bonds. Each of the two unhybridised p orbitals of both the carbon atoms overlaps sidewise to form two π bonds between the carbon atoms. So the triple bond between the two carbon atoms is made up of one sigma and two pi bonds as shown in Fig. 4.16.

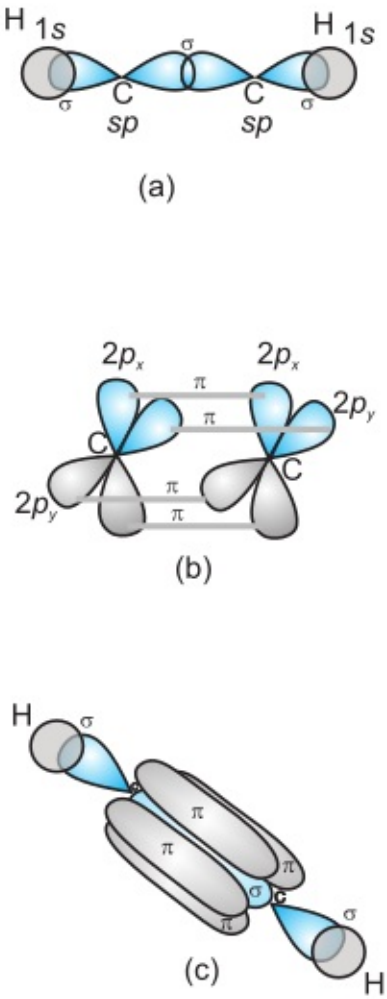


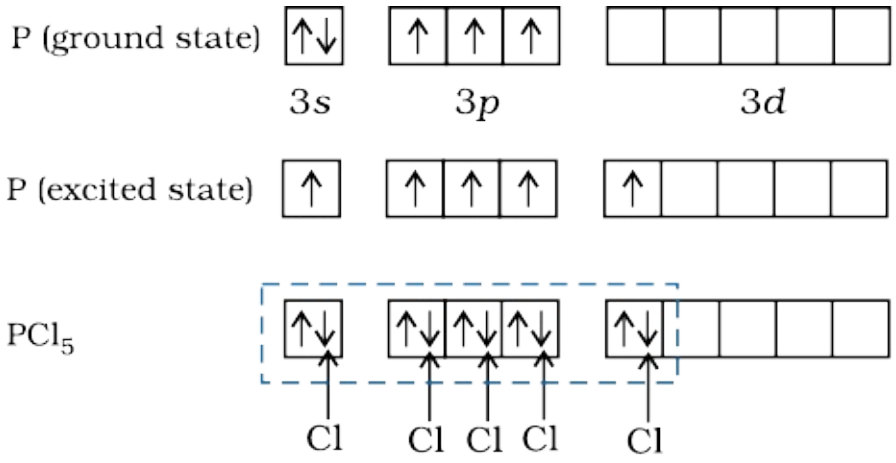
Fig.4.16 Formation of sigma and pi bonds in ethyne

The elements present in the third period contain d orbitals in addition to s and p orbitals. The energy of the 3d orbitals are comparable to the energy of the 3s and 3p orbitals. The energy of 3d orbitals are also comparable to those of 4s and 4p orbitals. As a consequence the hybridisation involving either 3s, 3p and 3d or 3d, 4s and 4p is possible. However, since the difference in energies of 3p and 4s orbitals is significant, no hybridisation involving 3p, 3d and 4s orbitals is possible.

Shape of molecules/ ions	Hybridisation type	Atomic orbitals	Examples
Square planar	dsp^2	$d+s+p(2)$	$[Ni(CN)_4]^{2-}$, $[Pt(Cl)_4]^{2-}$
Trigonal bipyramidal	sp^3d	$s+p(3)+d$	PF_5, PCl_5
Square pyramidal	sp^3d^2	$s+p(3)+d(2)$	BrF_5
Octahedral	sp^3d^2 d^2sp^3	$s+p(3)+d(2)$ $d(2)+s+p(3)$	SF_6, $[CrF_6]^{3-}$ $[Co(NH_3)_6]^{3+}$

The important hybridisation schemes involving s, p and d orbitals are summarised below:

(i) Formation of PCl_5 (sp^3d hybridisation): The ground state and the excited state outer electronic configurations of phosphorus (Z=15) are represented below.



sp^3d hybrid orbitals filled by electron pairs donated by five Cl atoms.

Now the five orbitals (i.e., one s, three p and one d orbitals) are available for hybridisation to yield a set of five sp^3d hybrid orbitals which are directed towards the five corners of a trigonal bipyramidal as depicted in

the Fig. 4.17.

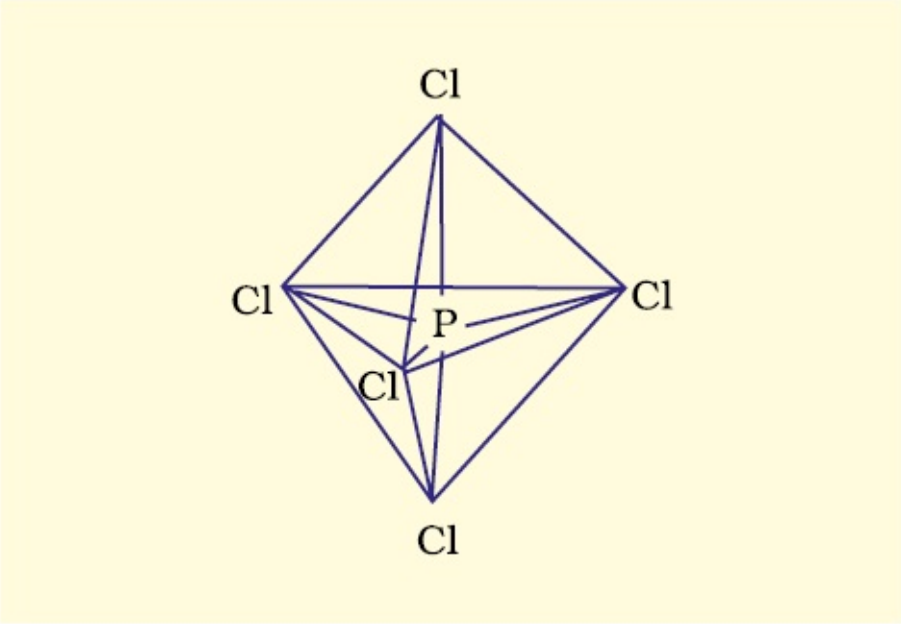
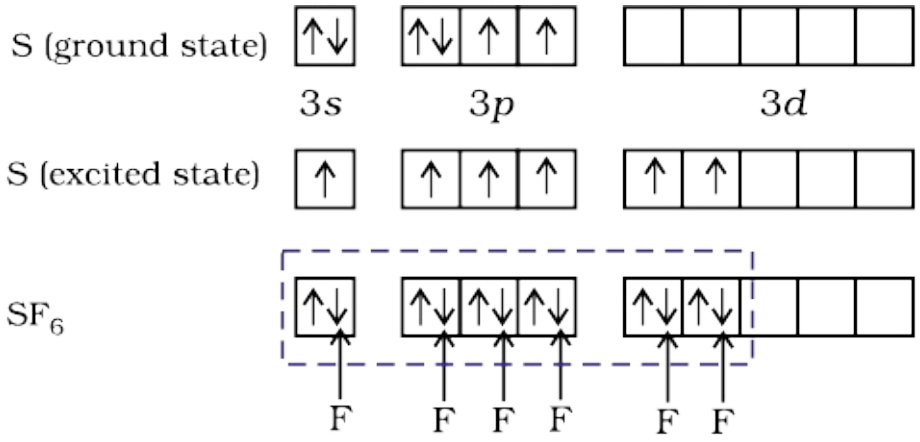


Fig. 4.17 Trigonal bipyramidal geometry of PCl_5 molecule

It should be noted that all the bond angles in trigonal bipyramidal geometry are not equivalent. In PCl_5 the five sp^3d orbitals of phosphorus overlap with the singly occupied p orbitals of chlorine atoms to form five P–Cl sigma bonds. Three P–Cl bond lie in one plane and make an angle of 120° with each other; these bonds are termed as equatorial bonds. The remaining two P–Cl bonds–one lying above and the other lying below the equatorial plane, make an angle of 90° with the plane. These bonds are called axial bonds. As the axial bond pairs suffer more repulsive interaction from the equatorial bond pairs, therefore axial bonds have been found to be slightly longer and hence slightly weaker than the equatorial bonds; which makes PCl_5 molecule more reactive.

(ii) Formation of SF_6 (sp^3d^2 hybridisation): In SF_6 the central sulphur atom has the ground state outer electronic configuration $3s^23p^4$. In the exited state the available six orbitals i.e., one s, three p and two d are

singly occupied by electrons. These orbitals hybridise to form six new sp^3d^2 hybrid orbitals, which are projected towards the six corners of a regular octahedron in SF_6. These six sp^3d^2 hybrid orbitals overlap with singly occupied orbitals of fluorine atoms to form six S–F sigma bonds. Thus SF_6 molecule has a regular octahedral geometry as shown in Fig. 4.18.



sp^3d^2 hybridisation

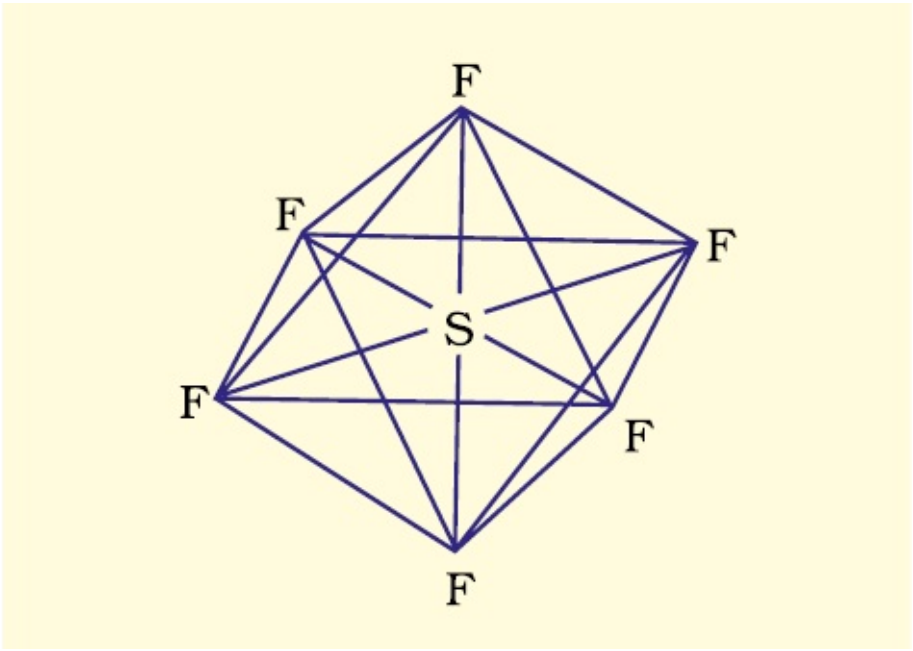


Fig. 4.18 Octahedral geometry of SF_6 molecule

4.7 Molecular Orbital Theory

Molecular orbital (MO) theory was developed by F. Hund and R.S. Mulliken in 1932. The salient features of this theory are :

(i) The electrons in a molecule are present in the various molecular orbitals as the electrons of atoms are present in the various atomic orbitals.

(ii) The atomic orbitals of comparable energies and proper symmetry combine to form molecular orbitals.

(iii) While an electron in an atomic orbital is influenced by one nucleus, in a molecular orbital it is influenced by two or more nuclei depending upon the number of atoms in the molecule. Thus, an atomic orbital is monocentric while a molecular orbital is polycentric.

(iv) The number of molecular orbital formed is equal to the number of combining atomic orbitals. When two atomic orbitals combine, two molecular orbitals are formed. One is known as **bonding molecular orbital** while the other is called **antibonding molecular orbital**.

(v) The bonding molecular orbital has lower energy and hence greater stability than the corresponding antibonding molecular orbital.

(vi) Just as the electron probability distribution around a nucleus in an atom is given by an atomic orbital, the electron probability distribution around a group of nuclei in a molecule is given by a molecular orbital.

(vii) The molecular orbitals like atomic orbitals are filled in accordance with the aufbau principle obeying the Pauli's exclusion principle and the Hund's rule.

4.7.1 Formation of Molecular Orbitals Linear Combination of Atomic Orbitals (LCAO)

According to wave mechanics, the atomic orbitals can be expressed by

wave functions (ψ 's) which represent the amplitude of the electron waves. These are obtained from the solution of Schrödinger wave equation. However, since it cannot be solved for any system containing more than one electron, molecular orbitals which are one electron wave functions for molecules are difficult to obtain directly from the solution of Schrödinger wave equation. To overcome this problem, an approximate method known as **linear combination of atomic orbitals (LCAO)** has been adopted.

Let us apply this method to the homonuclear diatomic hydrogen molecule. Consider the hydrogen molecule consisting of two atoms A and B. Each hydrogen atom in the ground state has one electron in 1s orbital. The atomic orbitals of these atoms may be represented by the wave functions ψ_A and ψ_B. Mathematically, the formation of molecular orbitals may be described by the linear combination of atomic orbitals that can take place by addition and by subtraction of wave functions of individual atomic orbitals as shown below :

$\psi_{MO} = \psi_A + \psi_B$

Therefore, the two molecular orbitals
σ and σ* are formed as :

$\sigma = \psi_A + \psi_B$

$\sigma^* = \psi_A - \psi_B$

The molecular orbital σ formed by the addition of atomic orbitals is called the **bonding molecular orbital** while the molecular orbital σ* formed by the subtraction of atomic orbital is called **antibonding molecular orbital** as depicted in Fig. 4.19.

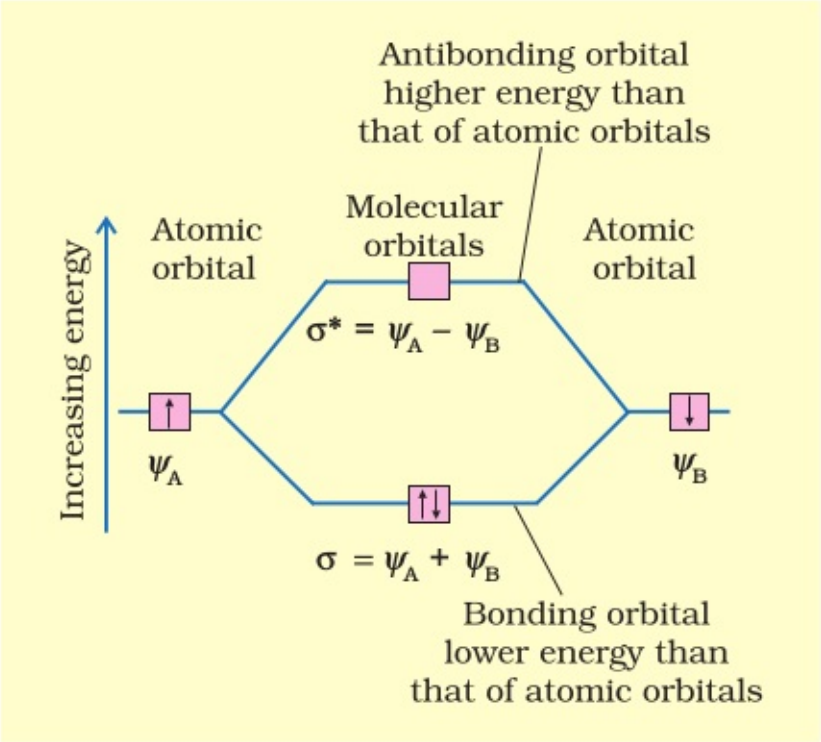


Fig.4.19 Formation of bonding (σ) and antibonding (σ) molecular orbitals by the linear combination of atomic orbitals ψ_A and ψ_B centered on two atoms A and B respectively.*

Qualitatively, the formation of molecular orbitals can be understood in terms of the constructive or destructive interference of the electron waves of the combining atoms. In the formation of bonding molecular orbital, the two electron waves of the bonding atoms reinforce each other due to constructive interference while in the formation of antibonding molecular orbital, the electron waves cancel each other due to destructive interference. As a result, the electron density in a bonding molecular orbital is located between the nuclei of the bonded atoms because of which the repulsion between the nuclei is very less while in case of an antibonding molecular orbital, most of the electron density is located away from the space between the nuclei. Infact, there is a nodal plane (on which the electron density is zero) between the nuclei and hence the repulsion between the nuclei is high. Electrons placed in a bonding molecular orbital tend to hold the nuclei together and stabilise a

molecule. Therefore, a bonding molecular orbital always possesses lower energy than either of the atomic orbitals that have combined to form it. In contrast, the electrons placed in the antibonding molecular orbital destabilise the molecule. This is because the mutual repulsion of the electrons in this orbital is more than the attraction between the electrons and the nuclei, which causes a net increase in energy.

It may be noted that the energy of the antibonding orbital is raised above the energy of the parent atomic orbitals that have combined and the energy of the bonding orbital has been lowered than the parent orbitals. The total energy of two molecular orbitals, however, remains the same as that of two original atomic orbitals.

4.7.2 Conditions for the Combination of Atomic Orbitals

The linear combination of atomic orbitals to form molecular orbitals takes place only if the following conditions are satisfied:

1. The combining atomic orbitals must have the same or nearly the same energy. This means that 1s orbital can combine with another 1s orbital but not with 2s orbital because the energy of 2s orbital is appreciably higher than that of 1s orbital. This is not true if the atoms are very different.

2. The combining atomic orbitals must have the same symmetry about the molecular axis. By convention z-axis is taken as the molecular axis. It is important to note that atomic orbitals having same or nearly the same energy will not combine if they do not have the same symmetry. For example, 2pz orbital of one atom can combine with 2pz orbital of the other atom but not with the 2px or 2py orbitals because of their different symmetries.

3. The combining atomic orbitals must overlap to the maximum extent. Greater the extent of overlap, the greater will be the electron-density between the nuclei of a molecular orbital.

4.7.3 Types of Molecular Orbitals

Molecular orbitals of diatomic molecules are designated as σ (sigma), π (pi), δ (delta), etc.

In this nomenclature, the **sigma (σ) molecular orbitals are symmetrical around the bond-axis while pi (π) molecular orbitals are not symmetrical**. For example, the linear combination of 1s orbitals centered on two nuclei produces two molecular orbitals which are symmetrical around the bond-axis. Such molecular orbitals are of the σ type and are designated as σ1s and σ*1s [Fig. 4.20(a),page 124]. **If internuclear axis is taken to be in the z-direction, it can be seen that a linear combination of $2p_z$- orbitals of two atoms also produces two sigma molecular orbitals designated as σ$2p_z$ and σ*$2p_z$**. [Fig. 4.20(b)]

Molecular orbitals obtained from $2p_x$ and $2p_y$ orbitals are not symmetrical around the bond axis because of the presence of positive lobes above and negative lobes below the molecular plane. Such molecular orbitals, are labelled as π and π* [Fig. 4.20(c)]. A π bonding MO has larger electron density above and below the inter-nuclear axis. The π* antibonding MO has a node between the nuclei.

4.7.4 Energy Level Diagram for Molecular Orbitals

We have seen that 1s atomic orbitals on two atoms form two molecular orbitals designated as σ1s and σ*1s. In the same manner, the 2s and 2p atomic orbitals (eight atomic orbitals on two atoms) give rise to the following eight molecular orbitals:

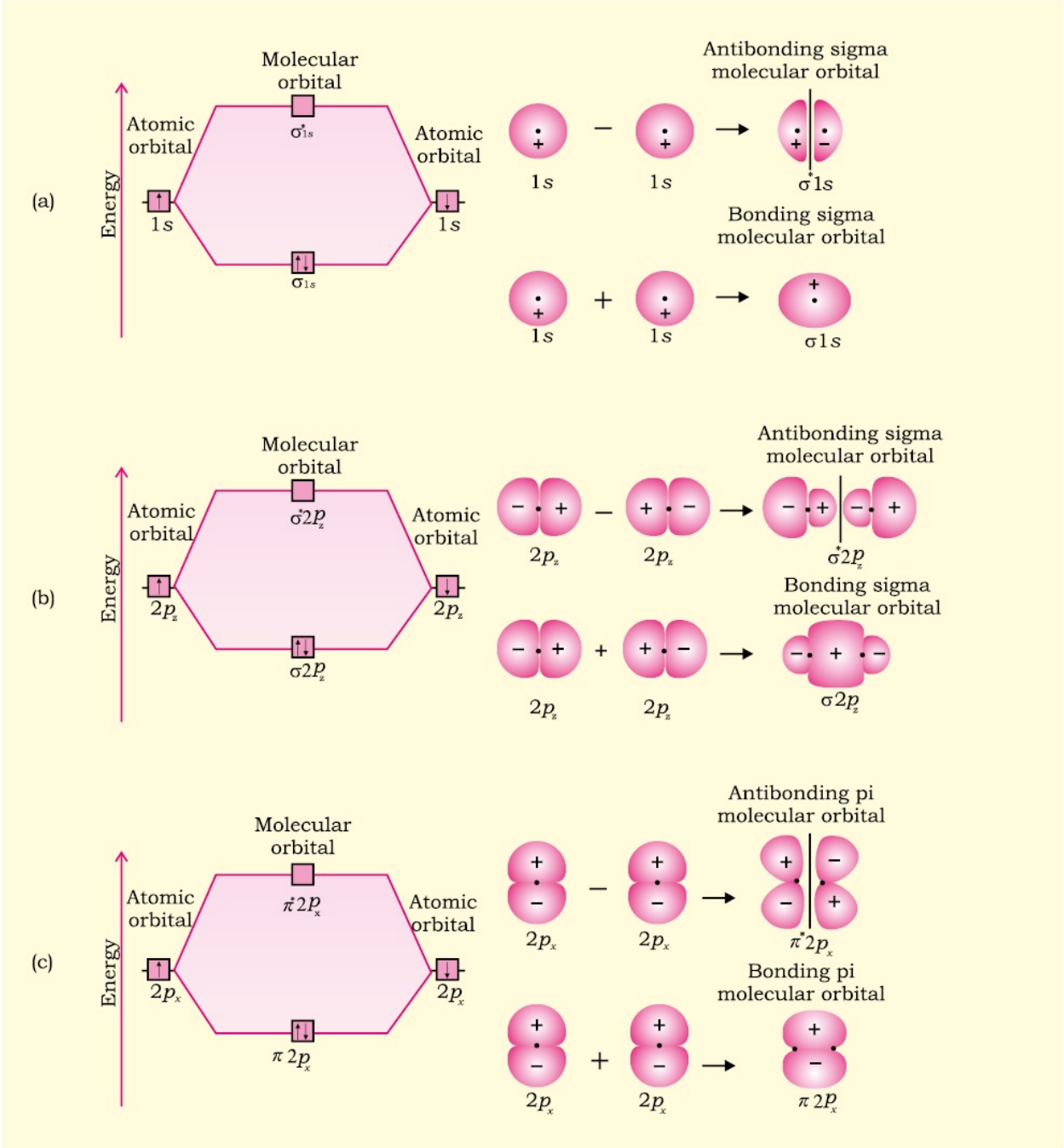


Fig. 4.20 Contours and energies of bonding and antibonding molecular orbitals formed through combinations of (a) 1s atomic orbitals; (b) $2p_Z$ atomic orbitals and (c) $2p_X$ atomic orbitals.

Antibonding	MOs	σ^*2s	σ^*2p_z	π^*2p_x	π^*2p_y
Bonding	MOs	$\sigma 2s$	$\sigma 2p_z$	$\pi 2p_x$	$\pi 2p_y$

The energy levels of these molecular

orbitals have been determined experimentally from spectroscopic data for homonuclear diatomic molecules of second row elements of the periodic table. The increasing order of energies of various molecular orbitals for O_2 and F_2 is given below:

$$\sigma 1s < \sigma^* 1s < \sigma 2s < \sigma^* 2s < \sigma 2p_z < (\pi 2p_x = \pi 2p_y) < (\pi^* 2p_x = \pi^* 2p_y) < \sigma^* 2p_z$$

However, this sequence of energy levels of molecular orbitals is not correct for the remaining molecules Li_2, Be_2, B_2, C_2, N_2. For instance, it has been observed experimentally that for molecules such as B_2, C_2, N_2, etc. the increasing order of energies of various molecular orbitals is

$$\sigma 1s < \sigma^* 1s < \sigma 2s < \sigma^* 2s < (\pi 2p_x = \pi 2p_y) < \sigma 2p_z < (\pi^* 2p_x = \pi^* 2p_y) < \sigma^* 2p_z$$

The important characteristic feature of this order is that the **energy of $\sigma 2p_z$ molecular orbital is higher than that of $\pi 2p_x$ and $\pi 2p_y$ molecular orbitals**.

4.7.5 Electronic Configuration and Molecular Behaviour

The distribution of electrons among various molecular orbitals is called the **electronic configuration of the molecule**. From the electronic configuration of the molecule, it is possible to get important information about the molecule as discussed below.

Stability of Molecules: If N_b is the number of electrons occupying bonding orbitals and N_a the number occupying the antibonding orbitals, then

(i) the molecule is stable if N_b is greater than N_a, and

(ii) the molecule is unstable if N_b is less than N_a.

In (i) more bonding orbitals are occupied and so the bonding influence is stronger and a stable molecule results. In (ii) the antibonding influence is stronger and therefore the molecule is unstable.

Bond order

Bond order (b.o.) is defined as one half the difference between the number of electrons present in the bonding and the antibonding orbitals i.e.,

Bond order (b.o.) = ½ (N_b–N_a)

The rules discussed above regarding the stability of the molecule can be restated in terms of bond order as follows: A positive bond order (i.e., $N_b > N_a$) means a stable molecule while a negative (i.e., $N_b<N_a$) or zero (i.e., $N_b = N_a$) bond order means an unstable molecule.

Nature of the bond

Integral bond order values of 1, 2 or 3 correspond to single, double or triple bonds respectively as studied in the classical concept.

Bond-length

The bond order between two atoms in a molecule may be taken as an approximate measure of the bond length. The bond length decreases as bond order increases.

Magnetic nature

If all the molecular orbitals in a molecule are doubly occupied, the substance is diamagnetic (repelled by magnetic field). However if one or more molecular orbitals are singly occupied it is paramagnetic (attracted by magnetic field), e.g., O_2 molecule.

4.8 BONDING IN SOME HOMONUCLEAR DIATOMIC MOLECULES

In this section we shall discuss bonding in some homonuclear diatomic molecules.

1. Hydrogen molecule (H_2): It is formed by the combination of two hydrogen atoms. Each hydrogen atom has one electron in 1s orbital. Therefore, in all there are two electrons in hydrogen molecule which are present in σ1s molecular orbital. So electronic configuration of hydrogen molecule is

$H_2 : (\sigma 1s)^2$

The bond order of H_2 molecule can be calculated as given below:

$$\text{Bond order} = \frac{N_b - N_a}{2} = \frac{2-0}{2} = 1$$

This means that the two hydrogen atoms are bonded together by a single covalent bond. The bond dissociation energy of hydrogen molecule has been found to be 438 kJ mol^{-1} and bond length equal to 74 pm. Since no unpaired electron is present in hydrogen molecule, therefore, it is diamagnetic.

2. Helium molecule (He_2): The electronic configuration of helium atom is $1s^2$. Each helium atom contains 2 electrons, therefore, in He_2 molecule there would be 4 electrons. These electrons will be accommodated in σ1s and σ*1s molecular orbitals leading to electronic configuration:

$He_2 : (\sigma 1s)^2 (\sigma^* 1s)^2$

Bond order of He_2 is ½(2 – 2) = 0

He_2 molecule is therefore unstable and does not exist.

Similarly, it can be shown that Be2 molecule $(\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma 2s)^2 (\sigma^* 2s)^2$ also does not exist.

3. Lithium molecule (Li_2): The electronic configuration of lithium is $1s^2$, $2s^1$. There are six electrons in Li_2. The electronic configuration of Li_2

molecule, therefore, is Li_2 : $(\sigma 1s)^2\ (\sigma^* 1s)^2\ (\sigma 2s)^2$

The above configuration is also written as $KK(\sigma 2s)^2$ where KK represents the closed K shell structure $(\sigma 1s)^2\ (\sigma^* 1s)^2$.

From the electronic configuration of Li_2 molecule it is clear that there are four electrons present in bonding molecular orbitals and two electrons present in antibonding molecular orbitals. Its bond order, therefore, is ½ (4 – 2) = 1. It means that Li_2 molecule is stable and since it has no unpaired electrons it should be diamagnetic. Indeed diamagnetic Li_2 molecules are known to exist in the vapour phase.

4. Carbon molecule (C_2): The electronic configuration of carbon is $1s^2\ 2s^2\ 2p^2$. There are twelve electrons in C_2. The electronic configuration of C_2 molecule, therefore, is

$$C_2 : (\sigma 1s)^2\ (\sigma^* 1s)^2\ (\sigma^* 2s)^2\ (\pi 2p_x^2 = \pi 2p_y^2)$$

$$\text{or } KK(\sigma 2s)^2(\sigma^* 2s)^2(\pi 2p_x^2 = \pi 2p_y^2)$$

The bond order of C_2 is ½ (8 – 4) = 2 and C_2 should be diamagnetic. Diamagnetic C_2 molecules have indeed been detected in vapour phase. It is important to note that double bond in C_2 consists of both pi bonds because of the presence of four electrons in two pi molecular orbitals. In most of the other molecules a double bond is made up of a sigma bond and a pi bond. In a similar fashion the bonding in N_2 molecule can be discussed.

5. Oxygen molecule (O_2): The electronic configuration of oxygen atom is $1s^2\ 2s^2\ 2p^4$. Each oxygen atom has 8 electrons, hence, in O_2 molecule there are 16 electrons. The electronic configuration of O_2 molecule, therefore, is

O_2: $(\sigma 1s)^2(\sigma^* 1s)^2(\sigma^* 2s)^2(\sigma^* 2s)^2(\sigma 2p_z)^2$

$\left(\pi 2p_x^{\,2} \equiv \pi 2p_y^{\,2}\right)\ \left(\pi^* 2p_x^{\,1} \equiv \pi^* 2p_y^{\,1}\right)$

$$O_2 : \begin{bmatrix} KK\,(\sigma 2s)^2(\sigma^* 2s)^2(\sigma 2p_z)^2 \\ \left(\pi 2p_x^2 \equiv \pi 2p_y^2\right),\left(\pi^* 2p_x^1 \equiv \pi^* 2p_y^1\right) \end{bmatrix}$$

From the electronic configuration of O_2 molecule it is clear that ten electrons are present in bonding molecular orbitals and six electrons are present in antibonding molecular orbitals. Its bond order, therefore, is

$$\text{Bond order} = \frac{1}{2}[N_b - N_a] = \frac{1}{2}[10-6] = 2$$

So in oxygen molecule, atoms are held by a double bond. Moreover, it may be noted that it contains two unpaired electrons in p^*2px and p^* 2py molecular orbitals, therefore, **O_2 molecule should be paramagnetic, a prediction that corresponds to experimental observation**. In this way, the theory successfully explains the paramagnetic nature of oxygen.

Similarly, the electronic configurations of other homonuclear diatomic molecules of the second row of the periodic table can be written. In Fig.4.21 are given the molecular orbital occupancy and molecular properties for B_2 through Ne_2. The sequence of MOs and their electron population are shown. The bond energy, bond length, bond order, magnetic properties and valence electron configuration appear below the orbital diagrams.

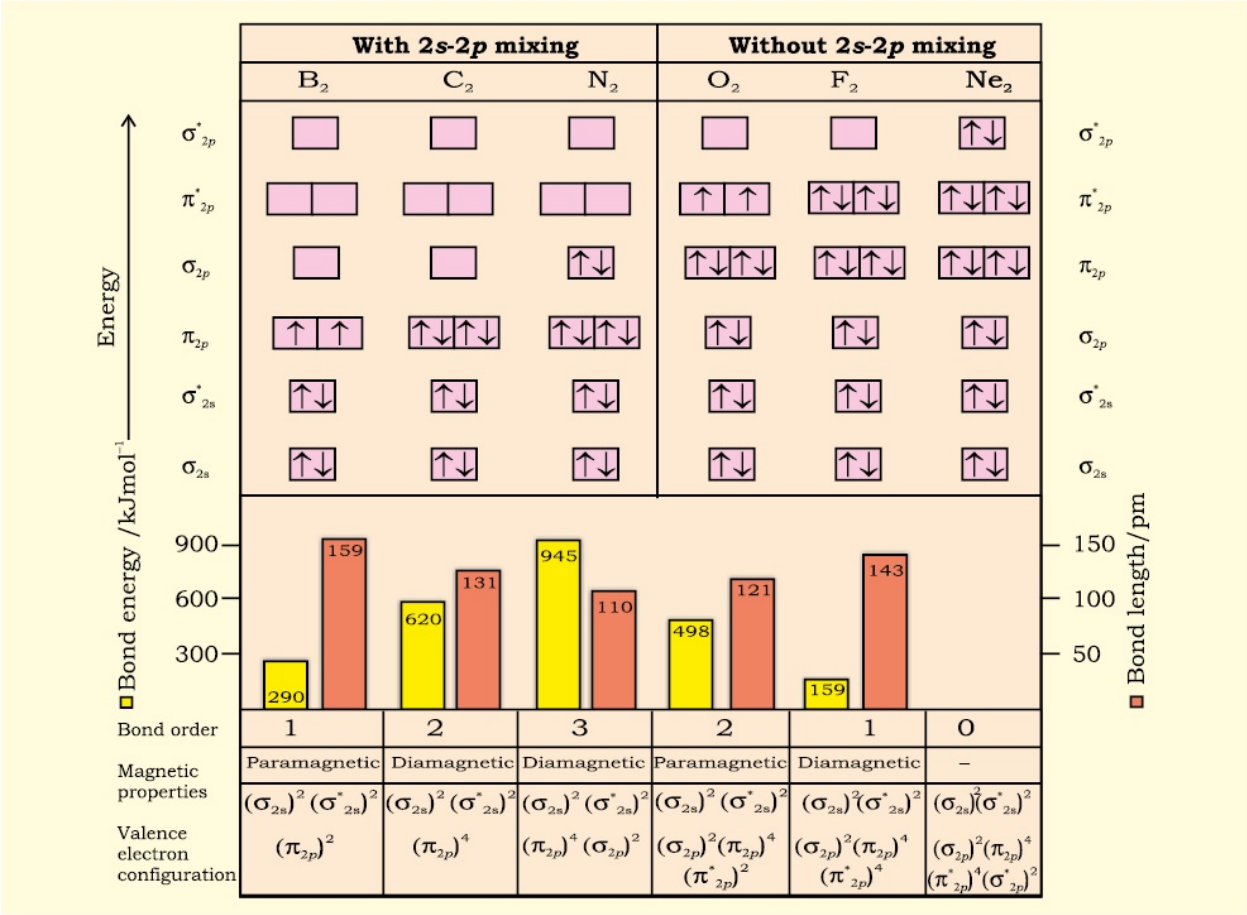


Fig. 4.21 MO occupancy and molecular properties for B_2 through Ne_2.

4.9 Hydrogen Bonding

Nitrogen, oxygen and fluorine are the higly electronegative elements. When they are attached to a hydrogen atom to form covalent bond, the electrons of the covalent bond are shifted towards the more electronegative atom. This partially positively charged hydrogen atom forms a bond with the other more electronegative atom. This bond is known as hydrogen bond and is weaker than the covalent bond. For example, in HF molecule, the hydrogen bond exists between hydrogen atom of one molecule and fluorine atom of another molecule as depicted below :

$$- - - H^{\delta+} - F^{\delta-} \; - - - \; H^{\delta+} - F^{\delta-} \; - - - \; H^{\delta+} - F^{\delta-}$$

Here, hydrogen bond acts as a bridge between two atoms which holds

one atom by covalent bond and the other by hydrogen bond. Hydrogen bond is represented by a dotted line (– – –) while a solid line represents the covalent bond. **Thus, hydrogen bond can be defined as the attractive force which binds hydrogen atom of one molecule with the electronegative atom (F, O or N) of another molecule.**

4.9.1 Cause of Formation of Hydrogen Bond

When hydrogen is bonded to strongly electronegative element 'X', the electron pair shared between the two atoms moves far away from hydrogen atom. As a result the hydrogen atom becomes highly electropositive with respect to the other atom 'X'. Since there is displacement of electrons towards X, the hydrogen acquires fractional positive charge (δ^+) while 'X' attain fractional negative charge (δ^-). This results in the formation of a polar molecule having electrostatic force of attraction which can be represented as :

$$H^{\delta+} - X^{\delta-} - - - H^{\delta+} - X^{\delta-} - - - H^{\delta+} - X^{\delta-}$$

The magnitude of H-bonding depends on the physical state of the compound. It is maximum in the solid state and minimum in the gaseous state. Thus, the hydrogen bonds have strong influence on the structure and properties of the compounds.

4.9.2 Types of H-Bonds

There are two types of H-bonds

(i) Intermolecular hydrogen bond

(ii) Intramolecular hydrogen bond

(1) Intermolecular hydrogen bond : It is formed between two different molecules of the same or different compounds. For example, H-bond in case of HF molecule, alcohol or water molecules, etc.

(2) Intramolecular hydrogen bond : It is formed when hydrogen atom is in between the two highly electronegative (F, O, N) atoms present within

the same molecule. For example, in o-nitrophenol the hydrogen is in between the two oxygen atoms.

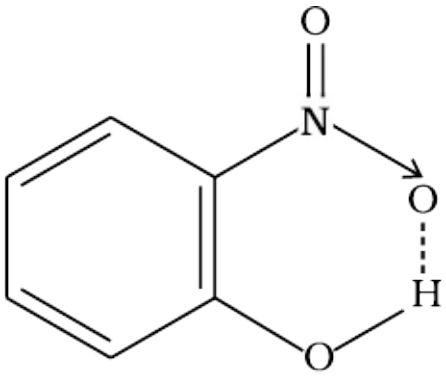


Fig. 4.22 Intramolecular hydrogen bonding in o-nitrophenol molecule

SUMMARY

Kössel's first insight into the mechanism of formation of electropositive and electronegative ions related the process to the attainment of noble gas configurations by the respective ions. Electrostatic attraction between ions is the cause for their stability. This gives the concept of **electrovalency**.

The first description of **covalent bonding** was provided by Lewis in terms of the sharing of electron pairs between atoms and he related the process to the attainment of noble gas configurations by reacting atoms as a result of sharing of electrons. The Lewis dot symbols show the number of valence electrons of the atoms of a given element and Lewis dot structures show pictorial representations of bonding in molecules.

An ionic compound is pictured as a three-dimensional aggregation of positive and negative ions in an ordered arrangement called the crystal lattice. In a crystalline solid there is a charge balance between the positive and negative ions. The crystal lattice is stabilized by the **enthalpy of lattice formation**.

While a single covalent bond is formed by sharing of an electron pair between two atoms, multiple bonds result from the sharing of two or three electron pairs. Some bonded atoms have additional pairs of electrons not involved in bonding. These are called lone-pairs of electrons. A

Lewis dot structure shows the arrangement of bonded pairs and lone pairs around each atom in a molecule. **Important parameters, associated with chemical bonds, like: bond length, bond angle, bond enthalpy, bond order and bond polarity have significant effect on the properties of compounds.**

A number of molecules and polyatomic ions cannot be described accurately by a single Lewis structure and a number of descriptions (representations) based on the same skeletal structure are written and these taken together represent the molecule or ion. This is a very important and extremely useful concept called **resonance**. The contributing structures or canonical forms taken together constitute the resonance hybrid which represents the molecule or ion.

The VSEPR model used for predicting the geometrical shapes of molecules is based on the assumption that electron pairs repel each other and, therefore, tend to remain as far apart as possible. According to this model, molecular geometry is determined by repulsions between lone pairs and lone pairs ; lone pairs and bonding pairs and bonding pairs and bonding pairs. The order of these repulsions being : lp-lp > lp-bp > bp-bp

The **valence bond (VB) approach** to covalent bonding is basically concerned with the energetics of covalent bond formation about which the Lewis and VSEPR models are silent. Basically the VB theory discusses bond formation in terms of overlap of orbitals. For example the formation of the H_2 molecule from two hydrogen atoms involves the overlap of the 1s orbitals of the two H atoms which are singly occupied. It is seen that the potential energy of the system gets lowered as the two H atoms come near to each other. At the equilibrium inter-nuclear distance (bond distance) the energy touches a minimum. Any attempt to bring the nuclei still closer results in a sudden increase in energy and consequent destabilization of the molecule. Because of orbital overlap the electron density between the nuclei increases which helps in bringing them closer. It is however seen that the actual bond enthalpy and bond length values are not obtained by overlap alone and other variables have to be taken into account.

For explaining the characteristic shapes of polyatomic molecules Pauling introduced the concept of **hybridisation of atomic orbitals**. sp,sp^2, sp^3 hybridizations of atomic orbitals of Be, B,C, N and O are used to explain the formation and geometrical shapes of molecules like $BeCl_2$, BCl_3, CH_4, NH_3 and H_2O. They also explain the formation of multiple bonds in molecules like C_2H_2

and C_2H_4.

The **molecular orbital (MO) theory** describes bonding in terms of the combination and arrangment of atomic orbitals to form molecular orbitals that are associated with the molecule as a whole. The number of molecular orbitals are always equal to the number of atomic orbitals from which they are formed. Bonding molecular orbitals increase electron density between the nuclei and are lower in energy than the individual atomic orbitals. Antibonding molecular orbitals have a region of zero electron density between the nuclei and have more energy than the individual atomic orbitals.

The electronic configuration of the molecules is written by filling electrons in the molecular orbitals in the order of increasing energy levels. As in the case of atoms, the Pauli exclusion principle and Hund's rule are applicable for the filling of molecular orbitals. Molecules are said to be stable if the number of elctrons in bonding molecular orbitals is greater than that in antibonding molecular orbitals.

Hydrogen bond is formed when a hydrogen atom finds itself between two highly electronegative atoms such as F, O and N. It may be intermolecular (existing between two or more molecules of the same or different substances) or intramolecular (present within the same molecule). Hydrogen bonds have a powerful effect on the structure and properties of many compounds.

EXERCISES

4.1 Explain the formation of a chemical bond.

4.2 Write Lewis dot symbols for atoms of the following elements : Mg, Na, B, O, N, Br.

4.3 Write Lewis symbols for the following atoms and ions:

S and S^{2-}; Al and Al^{3+}; H and H^-

4.4 Draw the Lewis structures for the following molecules and ions :

H_2S, $SiCl_4$, BeF_2, CO_3^{2-}, HCOOH

4.5 Define octet rule. Write its significance and limitations.

4.6 Write the favourable factors for the formation of ionic bond.

4.7 Discuss the shape of the following molecules using the VSEPR model:

$BeCl_2$, BCl_3, $SiCl_4$, AsF_5, H_2S, PH_3

4.8 Although geometries of NH_3 and H_2O molecules are distorted tetrahedral, bond angle in water is less than that of ammonia. Discuss.

4.9 How do you express the bond strength in terms of bond order ?

4.10 Define the bond length.

4.11 Explain the important aspects of resonance with reference to the CO_3^{2-} ion.

4.12 H_3PO_3 can be represented by structures 1 and 2 shown below. Can these two structures be taken as the canonical forms of the resonance hybrid representing H_3PO_3 ? If not, give reasons for the same.

4.13 Write the resonance structures for SO_3, NO_2 and NO_3^- .

4.14 Use Lewis symbols to show electron transfer between the following atoms to form cations and anions : (a) K and S (b) Ca and O (c) Al and N.

4.15 Although both CO_2 and H_2O are triatomic molecules, the shape of H_2O molecule is bent while that of CO_2 is linear. Explain this on the basis of dipole moment.

4.16 Write the significance/applications of dipole moment.

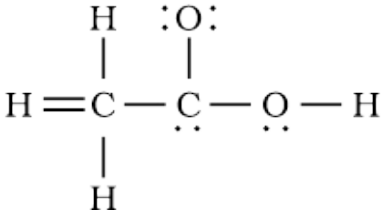
4.17 Define electronegativity. How does it differ from electron gain enthalpy ?

4.18 Explain with the help of suitable example polar covalent bond.

4.19 Arrange the bonds in order of increasing ionic character in the molecules: LiF, K_2O, N_2, SO_2 and ClF_3.

4.20 The skeletal structure of CH_3COOH as shown below is correct, but some of the bonds are shown incorrectly. Write the correct Lewis

structure for acetic acid.



4.21 Apart from tetrahedral geometry, another possible geometry for CH_4 is square planar with the four H atoms at the corners of the square and the C atom at its centre. Explain why CH_4 is not square planar ?

4.22 Explain why BeH_2 molecule has a zero dipole moment although the Be–H bonds are polar.

4.23 Which out of NH_3 and NF_3 has higher dipole moment and why ?

4.24 What is meant by hybridisation of atomic orbitals? Describe the shapes of sp, sp^2, sp^3 hybrid orbitals.

4.25 Describe the change in hybridisation (if any) of the Al atom in the following reaction.

$$AlCl_3 + Cl^- \rightarrow AlCl_4^-$$

4.26 Is there any change in the hybridisation of B and N atoms as a result of the following reaction?

$$BF_3 + NH_3 \rightarrow F_3B.NH_3$$

4.27 Draw diagrams showing the formation of a double bond and a triple bond between carbon atoms in C_2H_4 and C_2H_2 molecules.

4.28 What is the total number of sigma and pi bonds in the following molecules?

(a) C_2H_2 (b) C_2H_4

4.29 Considering x-axis as the internuclear axis which out of the following will not form a sigma bond and why?

(a) 1s and 1s

(b) 1s and $2p_x$;

(c) $2p_y$ and $2p_y$

(d) 1s and 2s.

4.30 Which hybrid orbitals are used by carbon atoms in the following molecules?

$CH_3–CH_3$; (b) $CH_3–CH=CH_2$; (c) CH_3-CH_2-OH; (d) CH_3-CHO (e) CH_3COOH

4.31 What do you understand by bond pairs and lone pairs of electrons? Illustrate by giving one exmaple of each type.

4.32 Distinguish between a sigma and a pi bond.

4.33 Explain the formation of H_2 molecule on the basis of valence bond theory.

4.34 Write the important conditions required for the linear combination of atomic orbitals to form molecular orbitals.

4.35 Use molecular orbital theory to explain why the Be_2 molecule does not exist.

4.36 Compare the relative stability of the following species and indicate their magnetic properties;

O_2, O_2^+, O_2 (superoxide), O_2^{2-} (peroxide)

4.37 Write the significance of a plus and a minus sign shown in representing the orbitals.

4.38 Describe the hybridisation in case of PCl_5. Why are the axial bonds longer as compared to equatorial bonds?

4.39 Define hydrogen bond. Is it weaker or stronger than the van der Waals forces?

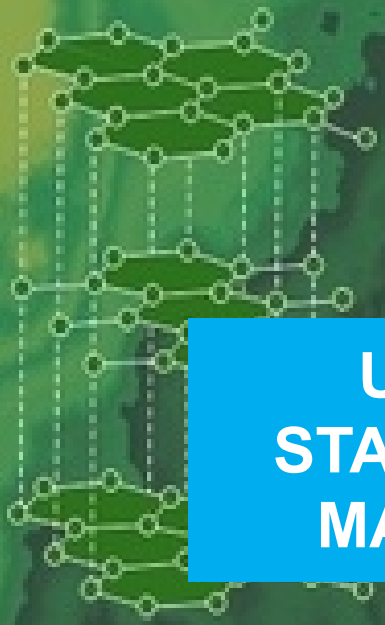
4.40 What is meant by the term bond order? Calculate the bond order of : N_2, O_2, O_2^+ and O_2^-.

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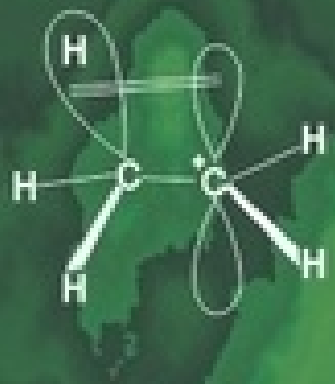
Textbook for Class XI



Unit 5
STATES OF MATTER

Chemistry

Part I



11082CH05

Unit 5

STATES OF MATTER

Objectives

After studying this unit you will be able to

- explain the existence of different states of matter in terms of balance between intermolecular forces and thermal energy of particles;
- explain the laws governing behaviour of ideal gases;
- apply gas laws in various real life situations;
- explain the behaviour of real gases;
- describe the conditions required for liquifaction of gases;
- realise that there is continuity in gaseous and liquid state;
- differentiate between gaseous state and vapours; and
- explain properties of liquids in terms of intermolecular attractions.

The snowflake falls, yet lays not long Its feath'ry grasp on Mother Earth Ere Sun returns it to the vapors Whence it came, Or to waters tumbling down the rocky slope.

Rod O' Connor

Introduction

In previous units we have learnt about the properties related to single particle of matter, such as atomic size, ionization enthalpy, electronic charge density, molecular shape and polarity, etc. Most of the observable characteristics of chemical systems with which we are familiar represent bulk properties of matter, i.e., the properties associated with a collection of a large number of atoms, ions or molecules. For example, an individual molecule of a liquid does not boil but the bulk boils. Collection of water molecules have wetting properties; individual molecules do not wet. Water can exist as ice, which is a solid; it can exist as liquid; or it can exist in the gaseous state as water vapour or steam. Physical properties of ice, water and steam are very different. In all the three states of water chemical composition of water remains the same i.e., H_2O. Characteristics of the three states of water depend on the energies of molecules and on the manner in which water molecules aggregate. Same is true for other substances also.

Chemical properties of a substance do not change with the change of its physical state; but rate of chemical reactions do depend upon the physical state. Many times in calculations while dealing with data of experiments we require knowledge of the state of matter. Therefore, it becomes necessary for a chemist to know the physical laws which govern the behaviour of matter in different states. In this unit, we will learn more about these three physical states of matter particularly liquid and gaseous states. To begin with, it is necessary to understand the nature of intermolecular forces, molecular interactions and effect of thermal energy on the motion of particles because a balance between these determines the state of a substance.

5.1 Intermolecular Forces

Intermolecular forces are the forces of attraction and repulsion between

interacting particles (atoms and molecules). This term does not include the electrostatic forces that exist between the two oppositely charged ions and the forces that hold atoms of a molecule together i.e., covalent bonds.

Attractive intermolecular forces are known as **van der Waals forces**, in honour of Dutch scientist Johannes van der Waals (1837-1923), who explained the deviation of real gases from the ideal behaviour through these forces. We will learn about this later in this unit. van der Waals forces vary considerably in magnitude and include dispersion forces or London forces, dipole-dipole forces, and dipole-induced dipole forces. A particularly strong type of dipole-dipole interaction is hydrogen bonding. **Only a few elements can participate in hydrogen bond formation, therefore it is treated as a separate category.** We have already learnt about this interaction in Unit 4.

At this point, it is important to note that attractive forces between an ion and a dipole are known as ion-dipole forces and these are not van der Waals forces. We will now learn about different types of van der Waals forces.

5.1.1 Dispersion Forces or London Forces

Atoms and nonpolar molecules are electrically symmetrical and have no dipole moment because their electronic charge cloud is symmetrically distributed. But a dipole may develop momentarily even in such atoms and molecules. This can be understood as follows. Suppose we have two atoms ‘A’ and ‘B’ in the close vicinity of each other (Fig. 5.1a). It may so happen that momentarily electronic charge distribution in one of the atoms, say ‘A’, becomes unsymmetrical i.e., the charge cloud is more on one side than the other (Fig. 5.1 b and c). This results in the development of instantaneous dipole on the atom ‘A’ for a very short time. This instantaneous or transient dipole distorts the electron density of the other atom ‘B’, which is close to it and as a consequence a dipole is induced in

the atom ‘B’.

The temporary dipoles of atom ‘A’ and ‘B’ attract each other. Similarly temporary dipoles are induced in molecules also. This force of attraction was first proposed by the German physicist Fritz London, and for this reason force of attraction between two temporary dipoles is known as **London force**. Another name for this force is **dispersion force**. These forces are always attractive and interaction energy is inversely proportional to the sixth power of the distance between two interacting particles (i.e., 1/r6 where r is the distance between two particles). These forces are important only at short distances (~500 pm) and their magnitude depends on the polarisability of the particle.

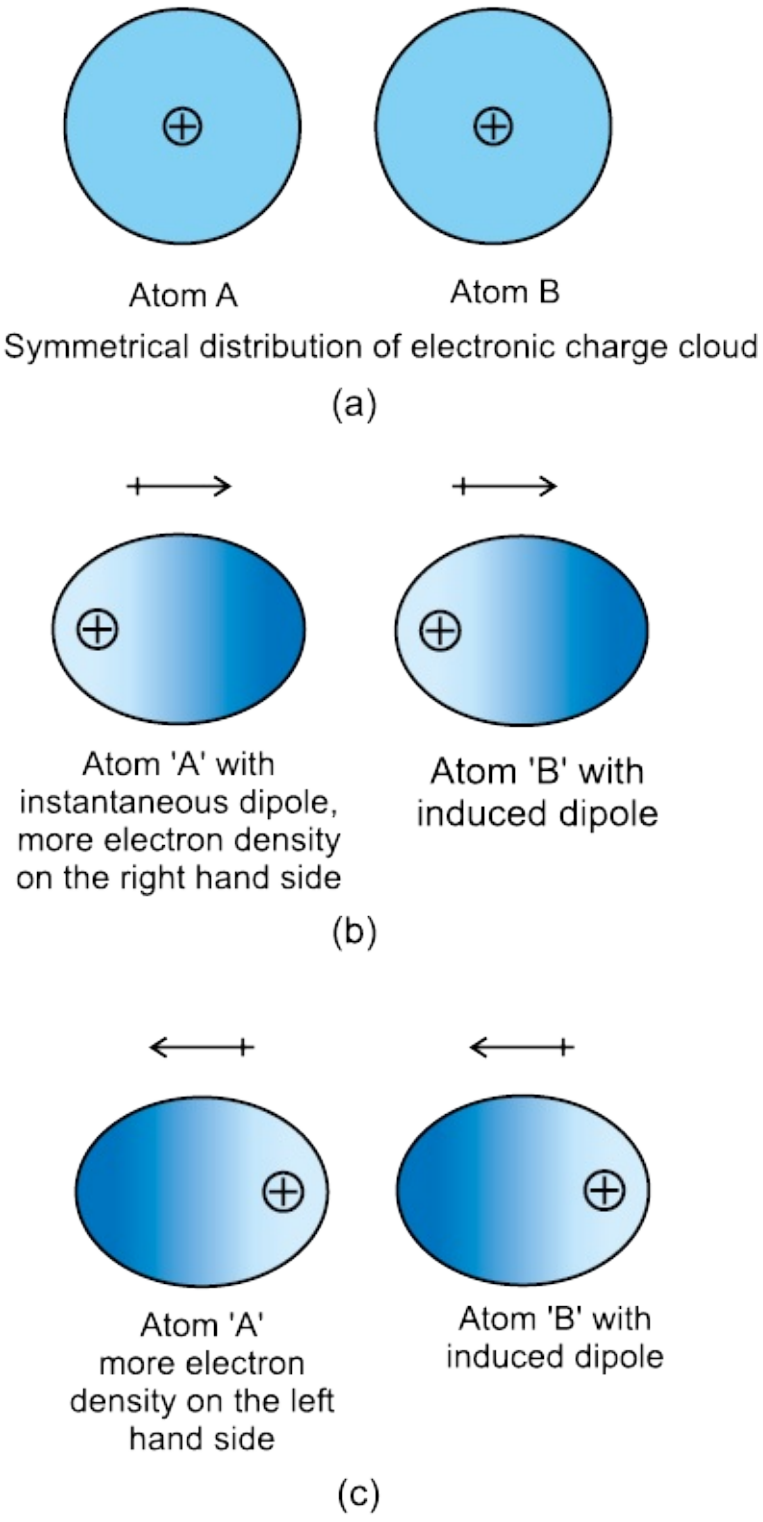


Fig. 5.1 Dispersion forces or London forces between atoms.

5.1.2 Dipole - Dipole Forces

Dipole-dipole forces act between the molecules possessing permanent

dipole. Ends of the dipoles possess “partial charges” and these charges are shown by Greek letter delta (δ). Partial charges are always less than the unit electronic charge (1.6×10–19 C). The polar molecules interact with neighbouring molecules. Fig 5.2 (a) shows electron cloud distribution in the dipole of hydrogen chloride and Fig. 5.2 (b) shows dipole-dipole interaction between two HCl molecules. This interaction is stronger than the London forces but is weaker than ion-ion interaction because only partial charges are involved. The attractive force decreases with the increase of distance between the dipoles. As in the above case here also, the interaction energy is inversely proportional to distance between polar molecules. Dipole-dipole interaction energy between stationary polar molecules (as in solids) is proportional to 1/r3 and that between rotating polar molecules is proportional to 1/r 6, where r is the distance between polar molecules. Besides dipole-dipole interaction, polar molecules can interact by London forces also. Thus cumulative effect is that the total of intermolecular forces in polar molecules increase.

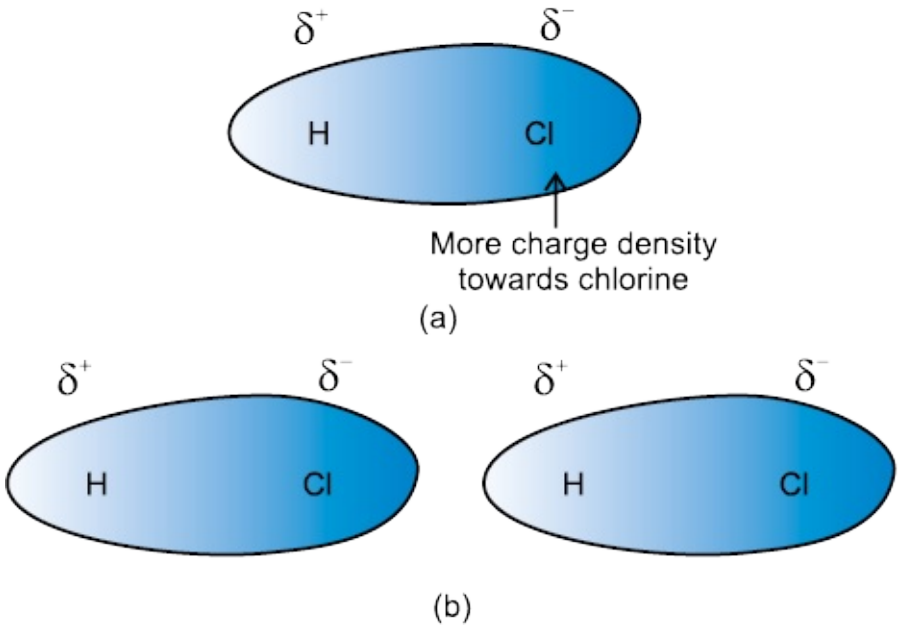


Fig. 5.2 (a) Distribution of electron cloud in HCl – a polar molecule, (b) Dipole-dipole interaction between two HCl molecules

5.1.3 Dipole–Induced Dipole Forces

This type of attractive forces operate between the polar molecules having permanent dipole and the molecules lacking permanent dipole. Permanent dipole of the polar molecule induces dipole on the electrically neutral molecule by deforming its electronic cloud (Fig. 5.3). Thus an induced dipole is developed in the other molecule. In this case also interaction energy is proportional to 1/r6 where r is the distance between two molecules. Induced dipole moment depends upon the dipole moment present in the permanent dipole and the polarisability of the electrically neutral molecule. We have already learnt in Unit 4 that molecules of larger size can be easily polarized. High polarisability increases the strength of attractive interactions.

In this case also cumulative effect of dispersion forces and dipole-induced dipole interactions exists.

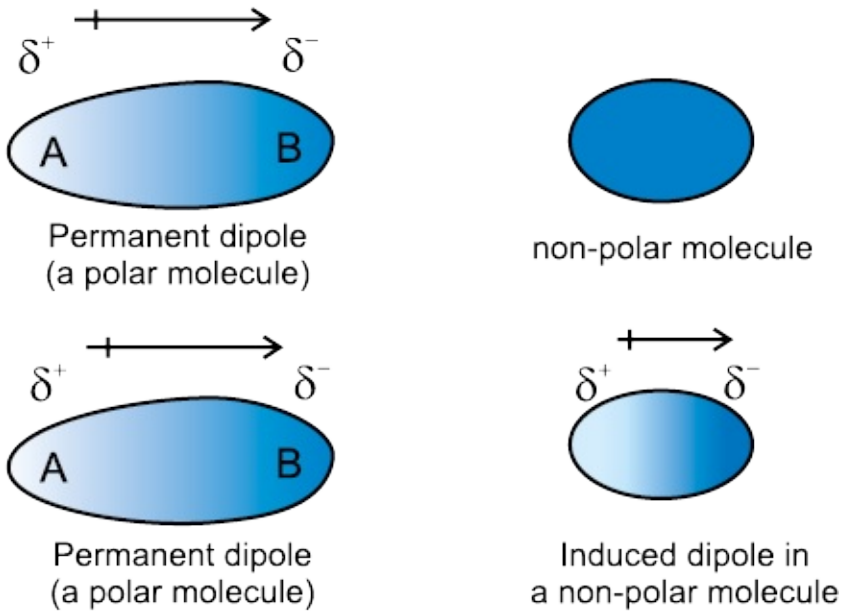


Fig. 5.3 Dipole - induced dipole interaction between permanent dipole and induced dipole

5.1.4 Hydrogen bond

As already mentioned in section (5.1); this is special case of dipole-dipole interaction. We have already learnt about this in Unit 4. This is found in

the molecules in which highly polar N–H, O–H or H–F bonds are present. Although hydrogen bonding is regarded as being limited to N, O and F; but species such as $\ddot{Cl}^-$ may also participate in hydrogen bonding. Energy of hydrogen bond varies between 10 to 100 kJ mol–1. This is quite a significant amount of energy; therefore, hydrogen bonds are powerful force in determining the structure and properties of many compounds, for example proteins and nucleic acids. Strength of the hydrogen bond is determined by the coulombic interaction between the lone-pair electrons of the electronegative atom of one molecule and the hydrogen atom of other molecule. Following diagram shows the formation of hydrogen bond.

$$\overset{\delta+}{\mathrm{H}}\!-\overset{\delta-}{\mathrm{F}}\cdots\overset{\delta+}{\mathrm{H}}\!-\overset{\delta-}{\mathrm{F}}$$

Intermolecular forces discussed so far are all attractive. **Molecules also exert repulsive forces** on one another. When two molecules are brought into close contact with each other, the repulsion between the electron clouds and that between the nuclei of two molecules comes into play. Magnitude of the repulsion rises very rapidly as the distance separating the molecules decreases. This is the reason that liquids and solids are hard to compress. In these states molecules are already in close contact; therefore they resist further compression; as that would result in the increase of repulsive interactions.

5.2 Thermal Energy

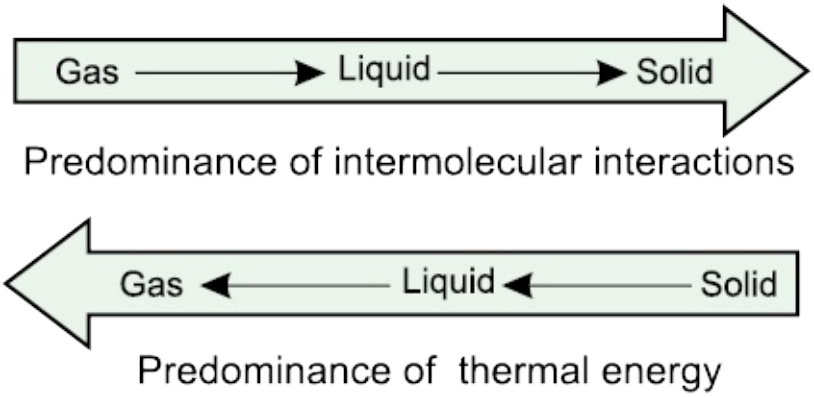
Thermal energy is the energy of a body arising from motion of its atoms or molecules. It is directly proportional to the temperature of the substance. It is the measure of average
kinetic energy of the particles of the matter and is thus responsible for

movement of particles. This movement of particles is called thermal motion.

5.3 Intermolecular Forces vs Thermal Interactions

We have already learnt that intermolecular forces tend to keep the molecules together but thermal energy of the molecules tends to keep them apart. Three states of matter are the result of balance between intermolecular forces and the thermal energy of the molecules.

When molecular interactions are very weak, molecules do not cling together to make liquid or solid unless thermal energy is reduced by lowering the temperature. Gases do not liquify on compression only, although molecules come very close to each other and intermolecular forces operate to the maximum. However, when thermal energy of molecules is reduced by lowering the temperature; the gases can be very easily liquified. Predominance of thermal energy and the molecular interaction energy of a substance in three states is depicted as follows :



We have already learnt the cause for the existence of the three states of matter. Now we will learn more about gaseous and liquid states and the laws which govern the behaviour of matter in these states. We shall deal with the solid state in class XII.

5.4 The Gaseous State

This is the simplest state of matter. Throughout our life we remain immersed in the ocean of air which is a mixture of gases. We spend our

life in the lowermost layer of the atmosphere called troposphere, which is held to the surface of the earth by gravitational force. The thin layer of atmosphere is vital to our life. It shields us from harmful radiations and contains substances like dioxygen, dinitrogen, carbon dioxide, water vapour, etc.

Let us now focus our attention on the behaviour of substances which exist in the gaseous state under normal conditions of temperature and pressure. A look at the periodic table shows that only eleven elements exist as gases under normal conditions

(Fig 5.4).

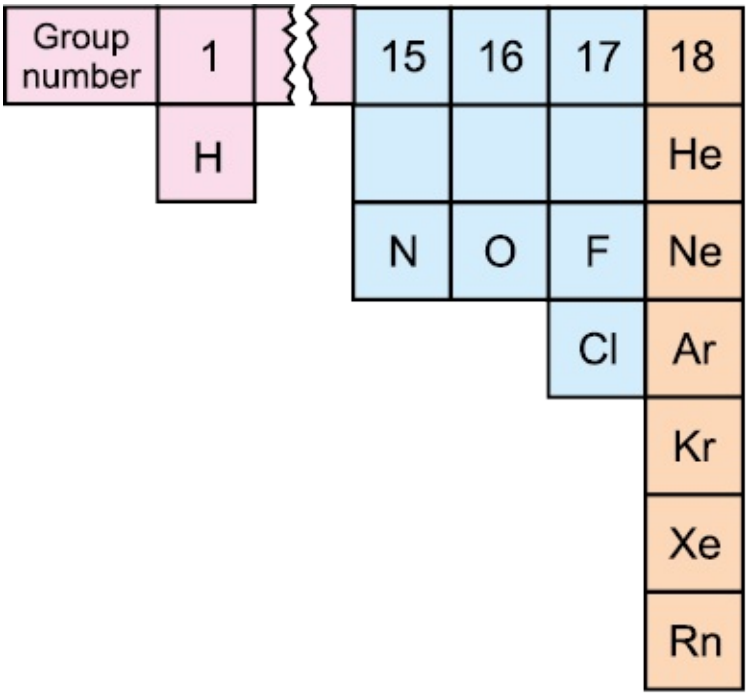


Fig. 5.4 Eleven elements that exist as gases

The gaseous state is characterized by the following physical properties.

• Gases are highly compressible.

• Gases exert pressure equally in all directions.

• Gases have much lower density than the solids and liquids.

• The volume and the shape of gases are not fixed. These assume volume and shape of the container.

• Gases mix evenly and completely in all proportions without any

mechanical aid.

Simplicity of gases is due to the fact that the forces of interaction between their molecules are negligible. Their behaviour is governed by same general laws, which were discovered as a result of their experimental studies. These laws are relationships between measurable properties of gases. Some of these properties like pressure, volume, temperature and mass are very important because relationships between these variables describe state of the gas. Interdependence of these variables leads to the formulation of gas laws. In the next section we will learn about gas laws.

5.5 The Gas Laws

The gas laws which we will study now are the result of research carried on for several centuries on the physical properties of gases. The first reliable measurement on properties of gases was made by Anglo-Irish scientist Robert Boyle in 1662. The law which he formulated is known as Boyle's Law. Later on attempts to fly in air with the help of hot air balloons motivated Jaccques Charles and Joseph Lewis Gay Lussac to discover additional gas laws. Contribution from Avogadro and others provided lot of information about gaseous state.

5.5.1 Boyle's Law (Pressure - Volume Relationship)

On the basis of his experiments, Robert Boyle reached to the conclusion that **at constant temperature, the pressure of a fixed amount** (i.e., number of moles n) **of gas varies inversely with its volume**. This is known as **Boyle's law**. Mathematically, it can be written as

$$p \propto \frac{1}{V} \quad (\text{at constant } T \text{ and } n) \qquad (5.1)$$

$$\Rightarrow p = k_1 \frac{1}{V} \qquad (5.2)$$

where k_1 is the proportionality constant. The value of constant k_1 depends upon the amount of the gas, temperature of the gas and the units in which p and V are expressed.

On rearranging equation (5.2) we obtain

$$pV = k_1 \quad (5.3)$$

It means that at constant temperature, product of pressure and volume of a fixed amount of gas is constant.

If a fixed amount of gas at constant temperature T occupying volume V_1 at pressure p_1 undergoes expansion, so that volume becomes V_2 and pressure becomes p_2, then according to Boyle's law :

$$p_1V_1 = p_2V_2 = \text{constant} \qquad (5.4)$$

$$\Rightarrow \frac{p_1}{p_2} = \frac{V_2}{V_1} \qquad (5.5)$$

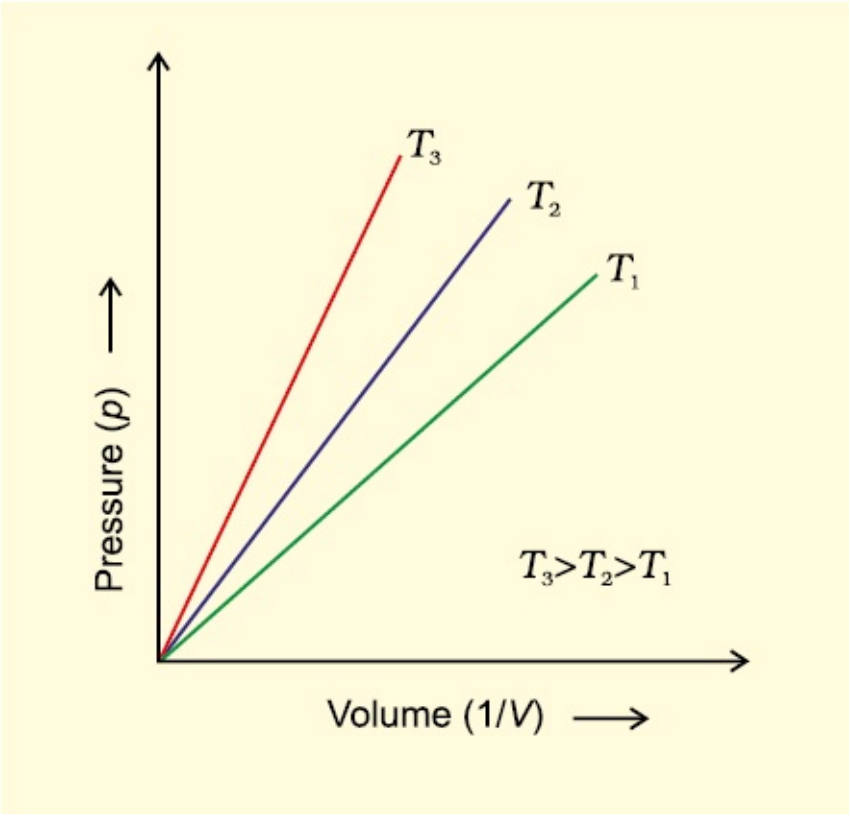


Fig. 5.5(a) Graph of pressure, p vs. Volume, V of a gas at different temperatures.

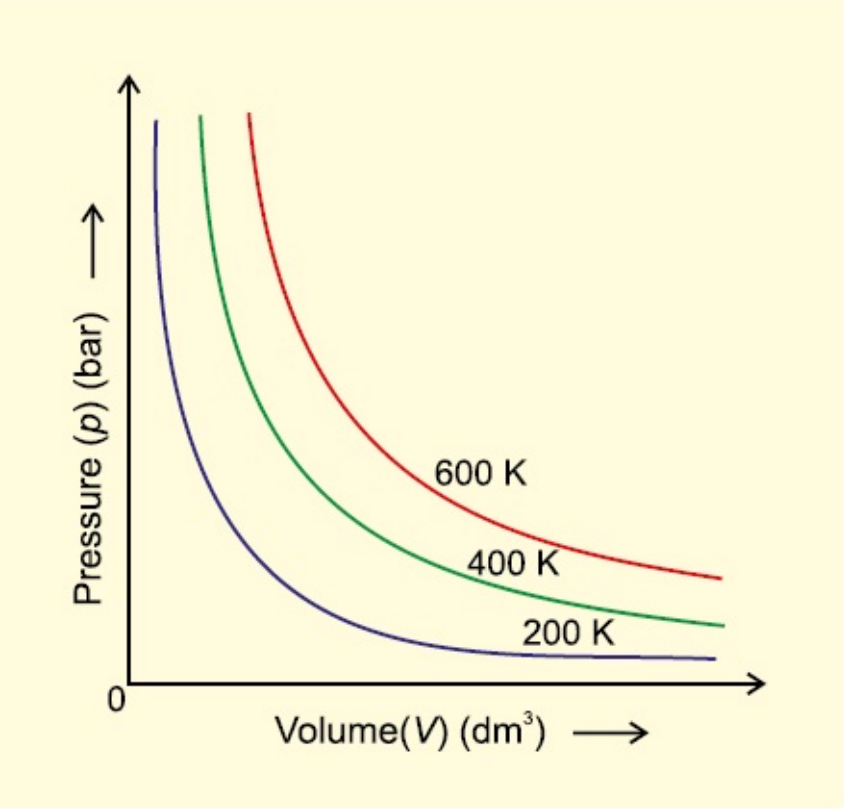


Fig. 5.5 (b) Graph of pressure of a gas, p vs. 1/v

Figure 5.5 shows two conventional ways of graphically presenting Boyle's law.

Fig. 5.5 (a) is the graph of equation (5.3) at different temperatures. The value of k1 for each curve is different because for a given mass of gas, it varies only with temperature. Each curve corresponds to a different constant temperature and is known as an isotherm (constant temperature plot). Higher curves correspond to higher temperature. It should be noted that volume of the gas doubles if pressure is halved. Table 5.1 gives effect of pressure on volume of 0.09 mol of CO2 at 300 K.

Fig 5.5 (b) represents the graph between p and $\frac{1}{V}$. It is a straight line passing through origin. However at high pressures, gases deviate from Boyle's law and under such conditions a straight line is not obtained in the graph.

Experiments of Boyle, in a quantitative manner prove that gases are highly compressible because when a given mass of a gas is compressed, the same number of molecules occupy a smaller space. This means that gases become denser at high pressure. A relationship can be obtained between density and pressure of a gas by using Boyle's law:

By definition, density 'd' is related to the mass 'm' and the volume 'V' by the relation $d = \frac{m}{V}$. If we put value of V in this equation from Boyle's law equation, we obtain the relationship.

Table 5.1 Effect of Pressure on the Volume of 0.09 mol CO2 Gas at 300 K.

Pressure/10^4 Pa	**Volume/10^{-3} m3**	**(1/V)/m^{-3}**	**pV/102 Pa m^3**
2.0	112.0	8.90	22.40
2.5	89.2	11.2	22.30
3.5	64.2	15.6	22.47
4.0	56.3	17.7	22.50
6.0	37.4	26.7	22.44
8.0	28.1	35.6	22.48
10.0	22.4	44.6	22.40

$$d = \left(\frac{m}{k_1}\right) p = k' p$$

This shows that at a constant temperature, pressure is directly proportional to the density of a fixed mass of the gas.

Problem 5.1

A balloon is filled with hydrogen at room temperature. It will burst if pressure exceeds 0.2 bar.

If at 1 bar pressure the gas occupies 2.27 L volume, upto what volume can the balloon be expanded ?

Solution

According to Boyle's Law p1V1 = p2V2

If p_1 is 1 bar, V_1 will be 2.27 L

$$\text{If } p_2 = 0.2 \text{ bar, then } V_2 = \frac{p_1 V_1}{p_2}$$

$$\Rightarrow V_2 = \frac{1\,\text{bar} \times 2.27\,\text{L}}{0.2\,\text{bar}} = 11.35\,\text{L}$$

Since balloon bursts at 0.2 bar pressure, the volume of balloon should be less than 11.35 L.

5.5.2 Charles' Law (Temperature - Volume Relationship)

Charles and Gay Lussac performed several experiments on gases independently to improve upon hot air balloon technology. Their investigations showed that for a fixed mass of a gas at constant pressure, volume of a gas increases on increasing temperature and decreases on cooling. They found that for each degree rise in temperature, volume of a gas increases by $\frac{1}{273.15}$ of the original volume of the gas at 0 °C. Thus if volumes of the gas at 0 °C and at t °C are V_0 and V_t respectively, then

$$V_t = V_0 + \frac{t}{273.15} V_0$$

$$\Rightarrow V_t = V_0 \left(1 + \frac{t}{273.15}\right)$$

$$\Rightarrow V_t = V_0 \left(\frac{273.15 + t}{273.15}\right) \qquad (5.6)$$

At this stage, we define a new scale of temperature such that t °C on new scale is given by T = 273.15 + t and 0 °C will be given by T_0 = 273.15. This new temperature scale is called the **Kelvin temperature scale** or

Absolute temperature scale.

Thus 0°C on the celsius scale is equal to 273.15 K at the absolute scale. Note that degree sign is not used while writing the temperature in absolute temperature scale, i.e., Kelvin scale. Kelvin scale of temperature is also called **Thermodynamic scale** of temperature and is used in all scientific works.

Thus we add 273 (more precisely 273.15) to the celsius temperature to obtain temperature at Kelvin scale.

If we write $T_t = 273.15 + t$ and $T_0 = 273.15$ in the equation (5.6) we obtain the relationship

$$V_t = V_0 \left(\frac{T_t}{T_0} \right)$$

$$\Rightarrow \frac{V_t}{V_0} = \frac{T_t}{T_0} \qquad (5.7)$$

Thus we can write a general equation as follows.

$$\frac{V_2}{V_1} = \frac{T_2}{T_1} \qquad (5.8)$$

$$\Rightarrow \frac{V_1}{T_1} = \frac{V_2}{T_2}$$

$$\Rightarrow \frac{V}{T} = \text{constant} = k_2 \qquad (5.9)$$

$$\text{Thus } V = k_2 T \qquad (5.10)$$

The value of constant k_2 is determined by the pressure of the gas, its amount and the units in which volume V is expressed.

Equation (5.10) is the mathematical expression for **Charles' law**, which states that **pressure remaining constant, the volume of a fixed mass of a gas is directly proportional to its absolute temperature.** Charles found that for all gases, at any given pressure, graph of volume vs temperature (in celsius) is a straight line and on extending to zero volume, each line intercepts the temperature axis at – 273.15 °C. Slopes of lines obtained at different pressure are different but at zero volume all the lines meet the temperature axis at – 273.15 °C (Fig. 5.6).

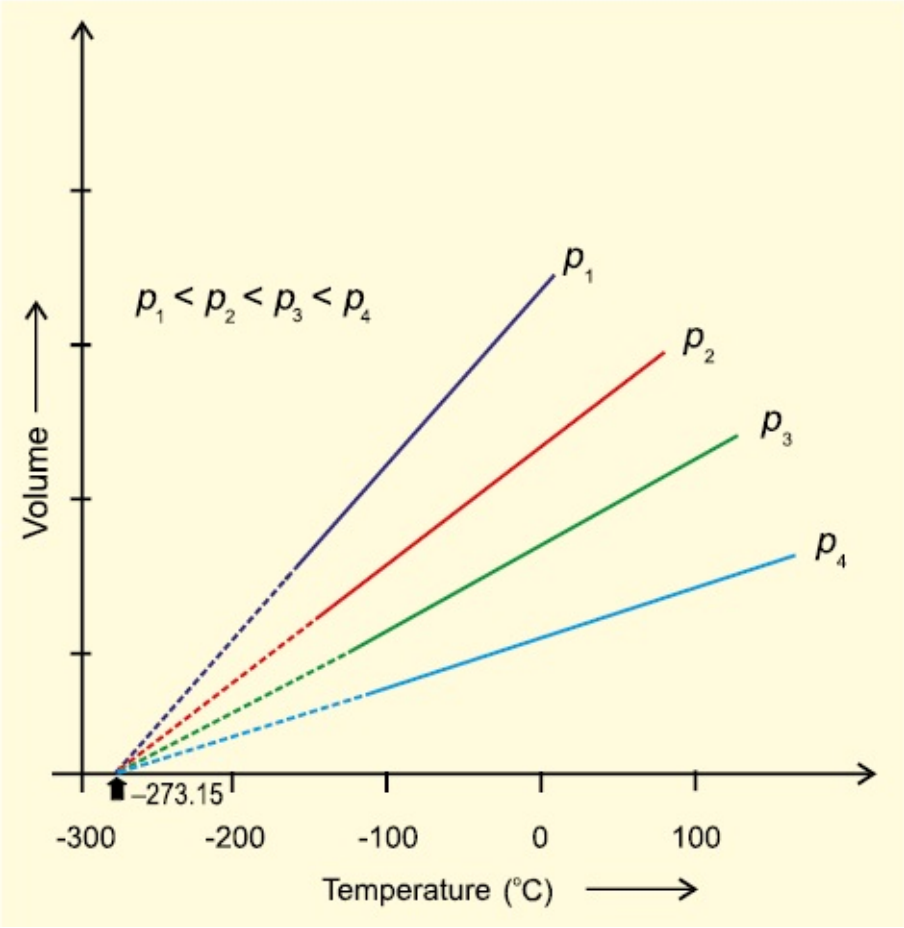


Fig. 5.6 Volume vs Temperature (°C) graph

Each line of the volume vs temperature graph is called **isobar.**

Observations of Charles can be interpreted if we put the value of t in

equation (5.6) as

– 273.15 °C. We can see that the volume of the gas at – 273.15 °C will be zero. This means that gas will not exist. In fact all the gases get liquified before this temperature is reached. The lowest hypothetical or imaginary temperature at which gases are supposed to occupy zero volume is called **Absolute zero**.

All gases obey Charles' law at very low pressures and high temperatures.

Problem 5.2

On a ship sailing in Pacific Ocean where temperature is 23.4°C, a balloon is filled with 2 L air. What will be the volume of the balloon when the ship reaches Indian ocean, where temperature is 26.1°C ?

Solution

V_1 = 2 L T_2 = 26.1 + 273

T_1 = (23.4 + 273) K = 299.1 K

= 296.4 K

From Charles law

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

$$\Rightarrow V_2 = \frac{V_1 T_2}{T_1}$$

$$\Rightarrow V_2 = \frac{2\,\text{L} \times 299.1\,\text{K}}{296.4\,\text{K}}$$

= 2L × 1.009

= 2.018L

5.5.3 Gay Lussac's Law (Pressure- Temperature Relationship)

Pressure in well inflated tyres of automobiles is almost constant, but on a hot summer day this increases considerably and tyre may burst if

pressure is not adjusted properly. During winters, on a cold morning one may find the pressure in the tyres of a vehicle decreased considerably. The mathematical relationship between pressure and temperature was given by Joseph Gay Lussac and is known as Gay Lussac's law. It states that **at constant volume, pressure of a fixed amount of a gas varies directly with the temperature.** Mathematically,

$$p \propto T$$

$$\Rightarrow \frac{p}{T} = \text{constant} = k_3$$

This relationship can be derived from Boyle's law and Charles' Law. Pressure vs temperature (Kelvin) graph at constant molar volume is shown in Fig. 5.7. Each line of this graph is called **isochore.**

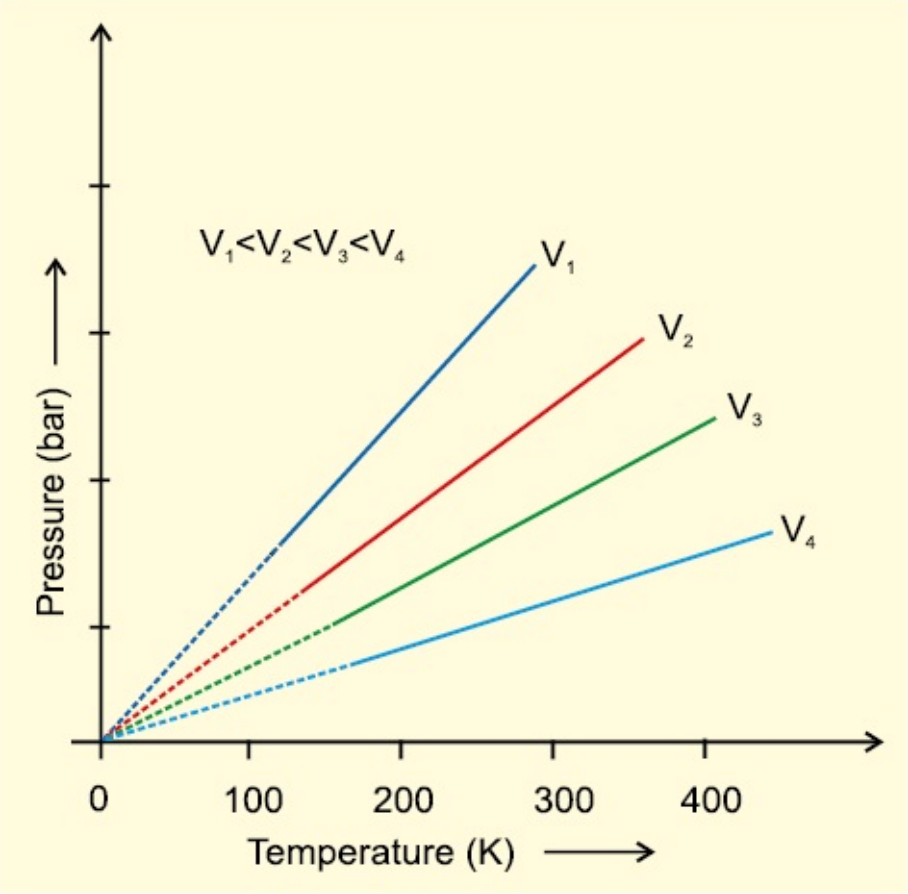


Fig. 5.7 Pressure vs temperature (K) graph (Isochores) of a gas.

5.5.4 Avogadro Law (Volume - Amount Relationship)

In 1811 Italian scientist Amedeo Avogadro tried to combine conclusions of Dalton's atomic theory and Gay Lussac's law of combining volumes (Unit 1) which is now known as Avogadro law. **It states that equal volumes of all gases under the same conditions of temperature and pressure contain equal number of molecules.** This means that as long as the temperature and pressure remain constant, the volume depends upon number of molecules of the gas or in other words amount of the gas. Mathematically we can write

$V \propto n$ where n is the number of moles of the gas.

$$\Rightarrow V = k_4 n \qquad (5.11)$$

The number of molecules in one mole of a gas has been determined to be 6.022 ×1023 and is known as **Avogadro constant**. You will find that this is the same number which we came across while discussing definition of a 'mole' (Unit 1).

Since volume of a gas is directly proportional to the number of moles; one mole of each gas at **standard temperature and pressure (STP)*** **will have same volume. Standard temperature and pressure means 273.15 K (0°C) temperature and 1 bar (i.e., exactly 10**5 **pascal) pressure. These values approximate freezing temperature of water and atmospheric pressure at sea level. At STP molar volume of an ideal gas or a combination of ideal gases is 22.71098 L mol**–1**.**

Molar volume of some gases is given in (Table 5.2).

Table 5.2 Molar volume in litres per mole of some gases at 273.15 K and 1 bar (STP).

Argon	22.37
Carbon dioxide	22.54
Dinitrogen	22.69
Dioxygen	22.69
Dihydrogen	22.72

Ideal gas	22.71

Number of moles of a gas can be calculated as follows

$$n = \frac{m}{M} \quad (5.12)$$

Where m = mass of the gas under investigation and M = molar mass
Thus,

$$V = k_4 \frac{m}{M} \quad (5.13)$$

Equation (5.13) can be rearranged as follows :

$$M = k_4 \frac{m}{M} = k_4 d \quad (5.14)$$

** The previous standard is still often used, and applies to all chemistry data more than decade old. In this definition STP denotes the same temperature of 0°C (273.15 K), but a slightly higher pressure of 1 atm (101.325 kPa). One mole of any gas of a combination of gases occupies 22.413996 L of volume at STP.*

Standard ambient temperature and pressure (SATP), conditions are also used in some scientific works. SATP conditions means 298.15 K and 1 bar (i.e., exactly 105 Pa). At SATP (1 bar and 298.15 K), the molar volume of an ideal gas is 24.789 L mol–1.

Here ‘d’ is the density of the gas. We can conclude from equation (5.14) that the density of a gas is directly proportional to its molar mass.
A gas that follows Boyle’s law, Charles’ law and Avogadro law strictly is called **an ideal gas**. Such a gas is hypothetical. It is assumed that intermolecular forces are not present between the molecules of an ideal gas. Real gases follow these laws only under certain specific conditions when forces of interaction are practically negligible. In all other situations these deviate from ideal behaviour. You will learn about the deviations later in this unit.

5.6 Ideal Gas Equation

The three laws which we have learnt till now can be combined together in a single equation which is known as **ideal gas equation**.

At constant T and n; $V \propto \frac{1}{p}$ **Boyle's Law**

At constant p and n; $V \propto T$ **Charles' Law**

At constant p and T; $V \propto n$ **Avogadro Law**

Thus,

$$V \propto \frac{nT}{p} \qquad (5.15)$$

$$\Rightarrow \quad V = \mathrm{R}\frac{nT}{p} \qquad (5.16)$$

where R is proportionality constant. On rearranging the equation (5.16) we obtain

$$pV = n\,\mathrm{R}T \qquad (5.17)$$

$$\Rightarrow \mathrm{R} = \frac{pV}{nT} \qquad (5.18)$$

R is called gas constant. It is same for all gases. Therefore it is also called **Universal Gas Constant**. Equation (5.17) is called **ideal gas equation.**

Equation (5.18) shows that the value of R depends upon units in which p, V and T are measured. If three variables in this equation are known, fourth can be calculated. From this equation we can see that at constant temperature and pressure n moles of any gas will have the same volume because $V = \frac{n\mathrm{R}T}{p}$ and n,R,T and p are constant. This equation will be

applicable to any gas, under those conditions when behaviour of the gas approaches ideal behaviour. Volume of one mole of an ideal gas under STP conditions (273.15 K and 1 bar pressure) is 22.710981 L mol–1. Value
of R for one mole of an ideal gas can be calculated under these conditions
as follows :

$$R = \frac{\left(10^5\,\text{Pa}\right)\left(22.71 \times 10^{-3}\text{m}^3\right)}{\left(1\,\text{mol}\right)\left(273.15\ \text{K}\right)}$$

= 8.314 Pa m3 K–1 mol–1
= 8.314 × 10–2 bar L K–1 mol–1
= 8.314 J K–1 mol–1
At STP conditions used earlier
(0 °C and 1 atm pressure), value of R is 8.20578 × 10–2 L atm K–1 mol–1.
Ideal gas equation is a relation between four variables and it describes the state of any gas, therefore, it is also called **equation of state**.
Let us now go back to the ideal gas equation. This is the relationship for the simultaneous variation of the variables. If temperature, volume and pressure of a fixed amount of gas vary from T_1, V_1 and p_1 to T_2, V_2 and p_2 then we can write

$$\frac{p_1V_1}{T_1} = nR \quad \text{and} \quad \frac{p_2V_2}{T_2} = nR$$

$$\Rightarrow \quad \frac{p_1V_1}{T_1} = \frac{p_2V_2}{T_2} \qquad (5.19)$$

Equation (5.19) is a very useful equation. If out of six, values of five variables are known, the value of unknown variable can be calculated from the equation (5.19). This equation is also known as **Combined gas**

law.

Problem 5.3

At 25°C and 760 mm of Hg pressure a gas occupies 600 mL volume. What will be its pressure at a height where temperature is 10°C and volume of the gas is 640 mL.

Solution

p_1 = 760 mm Hg, V_1= 600 mL

T_1 = 25 + 273 = 298 K

V_2 = 640 mL and T_2 = 10 + 273 = 283 K

According to Combined gas law

$$\frac{p_1V_1}{T_1} = \frac{p_2V_2}{T_2}$$

$$\Rightarrow p_2 = \frac{p_1V_1T_2}{T_1V_2}$$

$$\Rightarrow p_2 = \frac{(760\,\text{mm Hg}) \times (600\,\text{mL}) \times (283\,\text{K})}{(640\,\text{mL}) \times (298\,\text{K})}$$

5.6.1 Density and Molar Mass of a Gaseous Substance

Ideal gas equation can be rearranged as follows:

$$\frac{n}{V} = \frac{p}{RT}$$

Replacing n by $\frac{m}{M}$, we get

$$\frac{m}{MV} = \frac{p}{RT} \qquad (5.20)$$

$$\frac{d}{M} = \frac{p}{RT} \text{ (where } d \text{ is the density)} \qquad (5.21)$$

On rearranging equation (5.21) we get the relationship for calculating molar mass of a gas.

$$M = \frac{d\,RT}{p} \quad (5.22)$$

5.6.2 Dalton's Law of Partial Pressures

The law was formulated by John Dalton in 1801. It states that **the total pressure exerted by the mixture of non-reactive gases is equal to the sum of the partial pressures of individual gases** i.e., the pressures which these gases would exert if they were enclosed separately in the same volume and under the same conditions of temperature. In a mixture of gases, the pressure exerted by the individual gas is called **partial pressure**. Mathematically,

$$p_{Total} = p_1+p_2+p_3+\text{.....(at constant T, V)} \quad (5.23)$$

where p_{Total} is the total pressure exerted by the mixture of gases and p_1, p_2 , p_3 etc. are partial pressures of gases.

Gases are generally collected over water and therefore are moist. Pressure of dry gas can be calculated by subtracting vapour pressure of water from the total pressure of the moist gas which contains water vapours also. Pressure exerted by saturated water vapour is called **aqueous tension**. Aqueous tension of water at different temperatures is given in Table 5.3.

$$p_{Dry\ gas} = p_{Total} - \text{Aqueous tension} \quad (5.24)$$

Table 5.3 Aqueous Tension of Water (Vapour Pressure) as a Function of Temperature

Temp./K	Pressure/bar	Temp./K	Pressure/bar
273.15	0.0060	295.15	0.0260
283.15	0.0121	297.15	0.0295
288.15	0.0168	299.15	0.0331
291.15	0.0204	301.15	0.0372
293.15	0.0230	303.15	0.0418

Partial pressure in terms of mole fraction

Suppose at the temperature T, three gases, enclosed in the volume V, exert partial pressure p_1, p_2 and p_3 respectively, then,

$$p_1 = \frac{n_1 RT}{V} \quad (5.25)$$

$$p_2 = \frac{n_2 RT}{V} \quad (5.26)$$

$$p_3 = \frac{n_3 RT}{V} \quad (5.27)$$

where n_1 n_2 and n_3 are number of moles of these gases. Thus, expression for total pressure will be

$$p_{Total} = p_1 + p_2 + p_3$$

$$= n_1 \frac{RT}{V} + n_2 \frac{RT}{V} + n_3 \frac{RT}{V}$$

$$= (n_1 + n_2 + n_3) \frac{RT}{V} \qquad (5.28)$$

On dividing p_1 by p_{total} we get

$$\frac{p_1}{p_{total}} = \left(\frac{n_1}{n_1+n_2+n_3}\right) \frac{RTV}{RTV}$$

$$= \frac{n_1}{n_1+n_2+n_3} = \frac{n_1}{n} = x_1$$

where $n = n_1+n_2+n_3$

x_1 is called mole fraction of first gas.

Thus, $p_1 = x_1\ p_{total}$

Similarly for other two gases we can write

$p_2 = x_2\ p_{total}$ and $p_3 = x_3\ p_{total}$

Thus a general equation can be written as

$p_i = x_i\ p_{total}$ (5.29)

where p_i and x_i are partial pressure and mole fraction of ith gas respectively. If total pressure of a mixture of gases is known, the equation (5.29) can be used to find out pressure exerted by individual gases.

Problem 5.4

A neon-dioxygen mixture contains

70.6 g dioxygen and 167.5 g neon. If pressure of the mixture of gases in the cylinder is 25 bar. What is the partial pressure of dioxygen and neon in the mixture ?

Number of moles of neon

$$= \frac{167.5\,g}{20\,g\,mol^{-1}}$$

$$= 8.375\ mol$$

Mole fraction of dioxygen

$$= \frac{2.21}{2.21 + 8.375}$$

$$= \frac{2.21}{10.585}$$

$$= 0.21$$

$$\text{Mole fraction of neon} = \frac{8.375}{2.21 + 8.375}$$

= 0.79

Alternatively,

mole fraction of neon = 1– 0.21 = 0.79

Partial pressure = mole fraction ×

of a gas total pressure

⇒ Partial pressure = 0.21 × (25 bar)

of oxygen = 5.25 bar

Partial pressure = 0.79 × (25 bar)

of neon = 19.75 bar

5.7 Kinetic Energy and Molecular Speeds

Molecules of gases remain in continuous motion. While moving they collide with each other and with the walls of the container. This results in change of their speed and redistribution of energy. So the speed and energy of all the molecules of the gas at any instant are not the same. Thus, we can obtain only average value of speed of molecules. If there are n number of molecules in a sample and their individual speeds are u1, u2, …….un, then average speed of molecules uav can be calculated

as follows:

$$u_{av} = \frac{u_1 + u_2 + \ldots\ldots\ldots u_n}{n}$$

Maxwell and Boltzmann have shown that actual distribution of molecular speeds depends on temperature and molecular mass of a gas. Maxwell derived a formula for calculating the number of molecules possessing a particular speed. Fig. 5.8 shows schematic plot of number of molecules vs. molecular speed at two different temperatures T1 and T2 (T2 is higher than T1). The distribution of speeds shown in the plot is called Maxwell-Boltzmann distribution
of speeds.

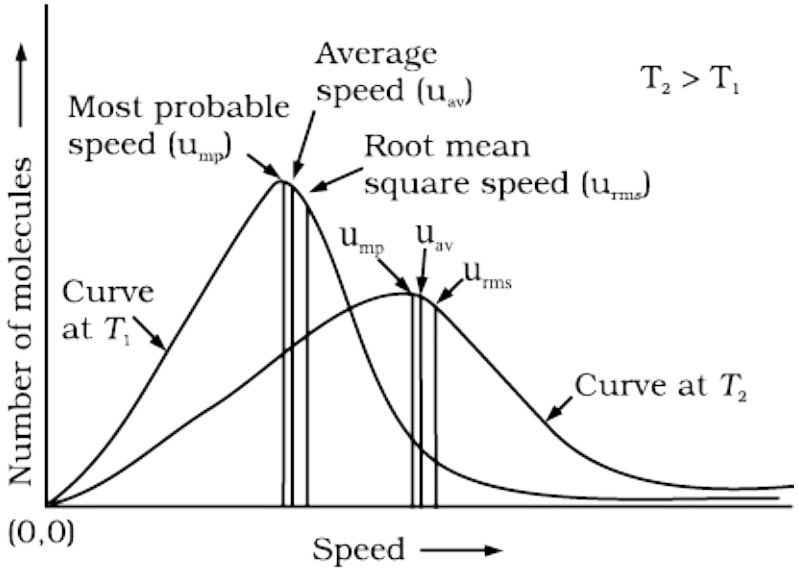


Fig. 5.8: Maxwell-Boltzmann distribution of speeds

The graph shows that number of molecules possessing very high and very low speed is very small. The maximum in the curve represents speed possessed by maximum number of molecules. This speed is called **most probable speed,** ump. This is very close to the average speed of the molecules. On increasing the temperature most probable speed increases. Also, speed distribution curve broadens at higher temperature. Broadening of the curve shows that number of molecules moving at higher speed increases. Speed distribution also depends upon

mass of molecules. At the same temperature, gas molecules with heavier mass have slower speed than lighter gas molecules. For example, at the same temperature lighter nitrogen molecules move faster than heavier chlorine molecules. Hence, at any given temperature, nitrogen molecules have higher value of most probable speed than the chlorine molecules. Look at the molecular speed distribution curve of chlorine and nitrogen given in Fig. 5.9. Though at a particular temperature the individual speed of molecules keeps changing, the distribution of speeds remains same.

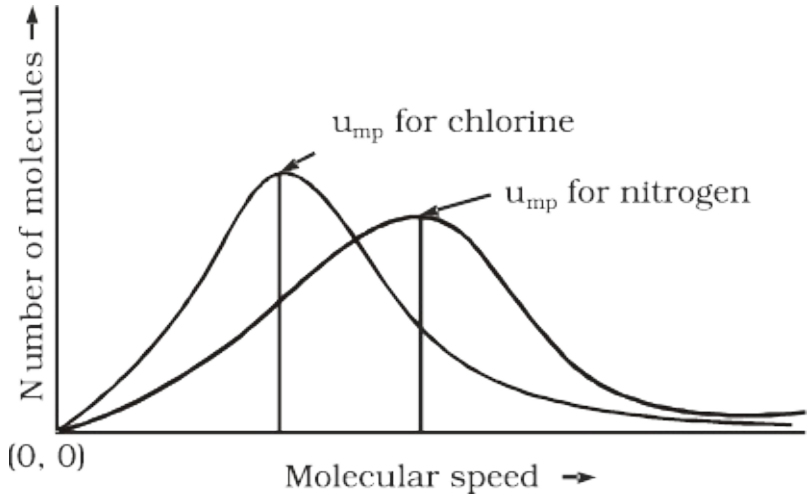


Fig. 5.9: Distribution of molecular speeds for chlorine and nitrogen at 300 K

We know that kinetic energy of a particle is given by the expression:

$$\text{Kinetic Energy} = \frac{1}{2}mu^2$$

Therefore, if we want to know average translational kinetic energy, $\frac{1}{2}m\overline{u^2}$, for the movement of a gas particle in a straight line, we require the value of mean of square of speeds, $\overline{u^2}$, of all molecules. This is represented as follows:

$$\overline{u^2} = \frac{u_1^2 + u_2^2 + \ldots\ldots\ldots u_n^2}{n}$$

The mean square speed is the direct measure of the average kinetic

energy of gas molecules. If we take the square root of the mean of the square of speeds then we get a value of speed which is different from most probable speed and average speed. This speed is called **root mean square speed** and is given by the expression as follows:

$$u_{rms} = \sqrt{\overline{u^2}}$$

Root mean square speed, average speed and the most probable speed have following relationship:

urms > uav > ump

The ratio between the three speeds is given below :

ump: uav : urms : : 1 : 1.128 : 1.224

5.8 Kinetic Molecular Theory of Gases

So far we have learnt the laws (e.g., Boyle's law, Charles' law etc.) which are concise statements of experimental facts observed in the laboratory by the scientists. Conducting careful experiments is an important aspect of scientific method and it tells us how the particular system is behaving under different conditions. However, once the experimental facts are established, a scientist is curious to know why the system is behaving in that way. For example, gas laws help us to predict that pressure increases when we compress gases but we would like to know what happens at molecular level when a gas is compressed ? A theory is constructed to answer such questions. A theory is a model (i.e., a mental picture) that enables us to better understand our observations. The theory that attempts to elucidate the behaviour of gases is known as kinetic molecular theory.

Assumptions or postulates of the kinetic-molecular theory of gases are given below. These postulates are related to atoms and molecules which cannot be seen, hence it is said to provide a microscopic model of gases.

• Gases consist of large number of identical particles (atoms or molecules) that are so small and so far apart on the average that the

actual volume of the molecules is negligible in comparison to the empty space between them. They are considered as point masses. This assumption explains the great compressibility of gases.

• There is no force of attraction between the particles of a gas at ordinary temperature and pressure. The support for this assumption comes from the fact that gases expand and occupy all the space available to them.

• Particles of a gas are always in constant and random motion. If the particles were at rest and occupied fixed positions, then a gas would have had a fixed shape which is not observed.

• Particles of a gas move in all possible directions in straight lines. During their random motion, they collide with each other and with the walls of the container. Pressure is exerted by the gas as a result of collision of the particles with the walls of the container.

• Collisions of gas molecules are perfectly elastic. This means that total energy of molecules before and after the collision remains same. There may be exchange of energy between colliding molecules, their individual energies may change, but the sum of their energies remains constant. If there were loss of kinetic energy, the motion of molecules will stop and gases will settle down. This is contrary to what is actually observed.

• At any particular time, different particles in the gas have different speeds and hence different kinetic energies. This assumption is reasonable because as the particles collide, we expect their speed to change. Even if initial speed of all the particles was same, the molecular collisions will disrupt this uniformity. Consequently, the particles must have different speeds, which go on changing constantly. It is possible to show that though the individual speeds are changing, the distribution of speeds remains constant at a particular temperature.

• If a molecule has variable speed, then it must have a variable kinetic energy. Under these circumstances, we can talk only about average kinetic energy. In kinetic theory, it is assumed that average kinetic energy

of the gas molecules is directly proportional to the absolute temperature. It is seen that on heating a gas at constant volume, the pressure increases. On heating the gas, kinetic energy of the particles increases and these strike the walls of the container more frequently, thus, exerting more pressure.

Kinetic theory of gases allows us to derive theoretically, all the gas laws studied in the previous sections. Calculations and predictions based on kinetic theory of gases agree very well with the experimental observations and thus establish the correctness of this model.

5.9 Behaviour of real gases: Deviation from ideal gas behaviour

Our theoritical model of gases corresponds very well with the experimental observations. Difficulty arises when we try to test how far the relation pV = nRT reproduce actual pressure-volume-temperature relationship

of gases. To test this point we plot pV vs p plot of gases because at constant temperature, pV will be constant (Boyle's law) and pV vs p graph at all pressures will be a straight line parallel to x-axis. Fig. 5.10 shows such a plot constructed from actual data for several gases at 273 K.

It can be seen easily that at constant temperature pV vs p plot for real gases is not a straight line. There is a significant deviation from ideal behaviour. Two types of curves are seen. In the curves for dihydrogen and helium, as the pressure increases the value of pV also increases. The second type of plot is seen in the case of other gases like carbon monoxide and methane. In these plots first there is a negative deviation from ideal behaviour, the pV value decreases with increase in pressure and reaches to a minimum value characteristic of a gas. After that pV value starts increasing. The curve then crosses the line for ideal gas and after that shows positive deviation continuously. It is thus, found that real

gases do not follow ideal gas equation perfectly under all conditions.

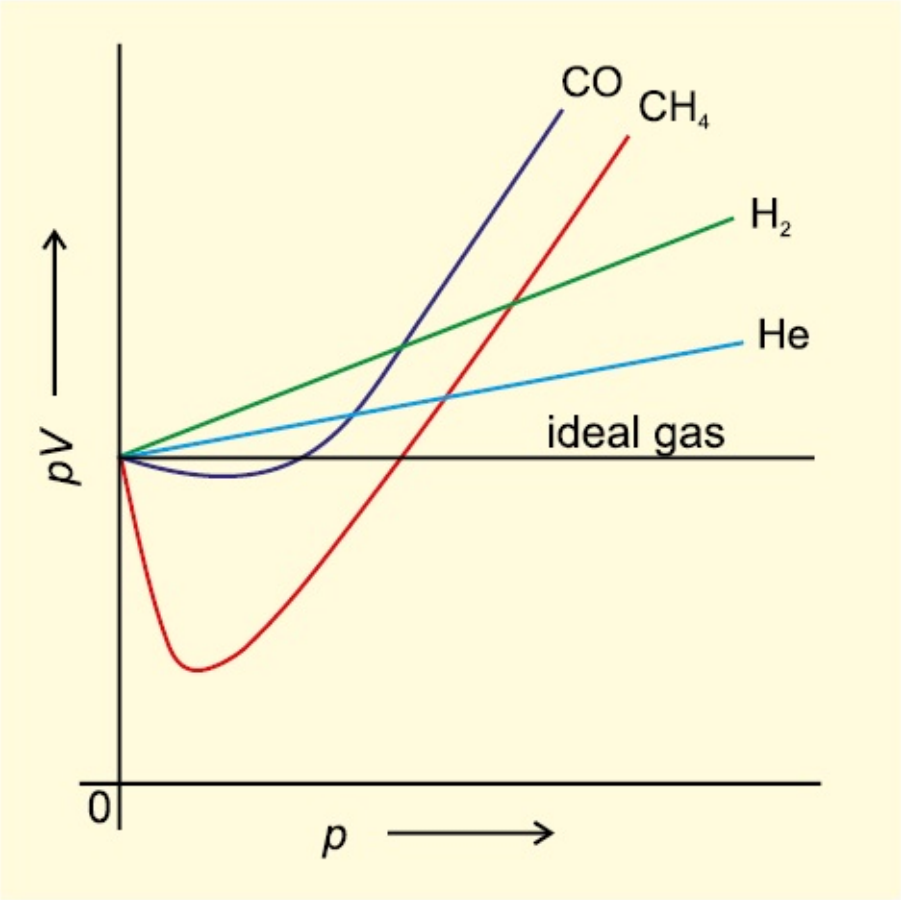


Fig. 5.10 Plot of pV vs p for real gas and ideal gas

Deviation from ideal behaviour also becomes apparent when pressure vs volume plot is drawn. The pressure vs volume plot of experimental data (real gas) and that theoretically calculated from Boyle's law (ideal gas) should coincide. Fig 5.11 shows these plots. It is apparent that at very high pressure the measured volume is more than the calculated volume. At low pressures, measured and calculated volumes approach each other.

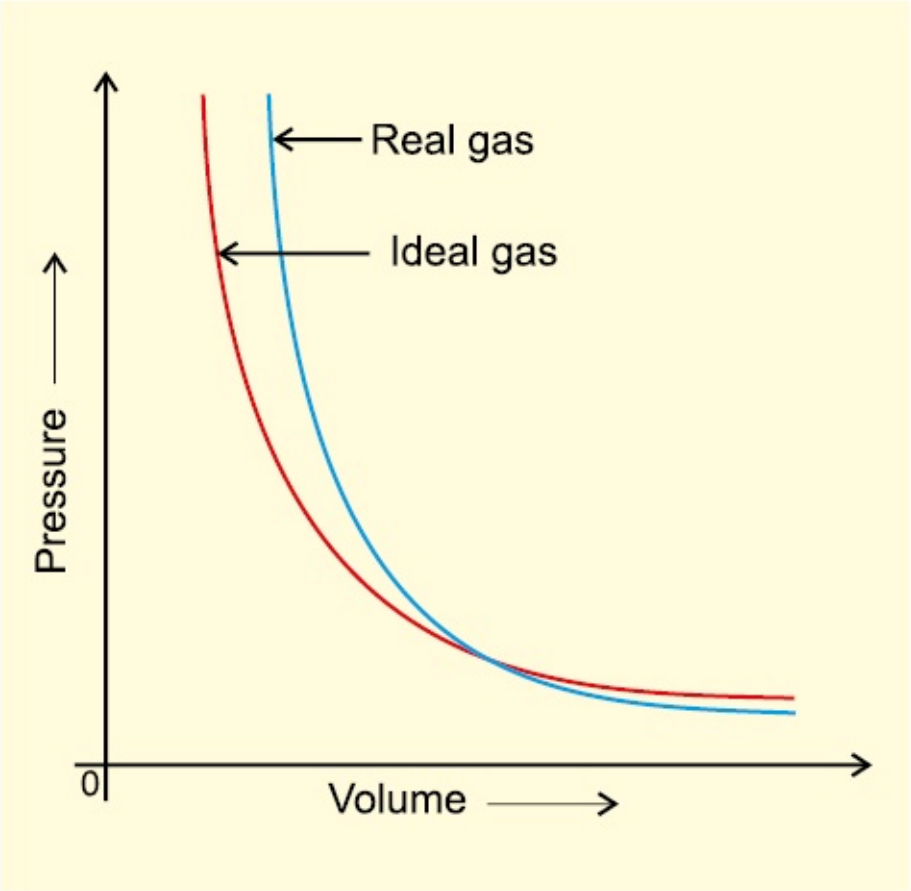


Fig. 5.11 Plot of pressure vs volume for real gas and ideal gas

It is found that real gases do not follow, Boyle's law, Charles law and Avogadro law perfectly under all conditions. Now two questions arise.

(i) Why do gases deviate from the ideal behaviour?

(ii) What are the conditions under which gases deviate from ideality?

We get the answer of the first question if we look into postulates of kinetic theory once again. We find that two assumptions of the kinetic theory do not hold good. These are

(a) There is no force of attraction between the molecules of a gas.

(b) Volume of the molecules of a gas is negligibly small in comparison to the space occupied by the gas.

If assumption (a) is correct, the gas will never liquify. However, we know that gases do liquify when cooled and compressed. Also, liquids formed are very difficult to compress. This means that forces of repulsion are

powerful enough and prevent squashing of molecules in tiny volume. If assumption (b) is correct, the pressure vs volume graph of experimental data (real gas) and that theoritically calculated from Boyles law (ideal gas) should coincide.

Real gases show deviations from ideal gas law because molecules interact with each other. At high pressures molecules of gases are very close to each other. Molecular interactions start operating. At high pressure, molecules do not strike the walls of the container with full impact because these are dragged back by other molecules due to molecular attractive forces. This affects the pressure exerted by the molecules on the walls of the container. Thus, the pressure exerted by the gas is lower than the pressure exerted by the ideal gas.

$$p_{ideal} = p_{real} + \frac{an^2}{V^2} \quad (5.30)$$

Here, a is a constant.

Repulsive forces also become significant. Repulsive interactions are short-range interactions and are significant when molecules are almost in contact. This is the situation at high pressure. The repulsive forces cause the molecules to behave as small but impenetrable spheres. The volume occupied by the molecules also becomes significant because instead of moving in volume V, these are now restricted to volume (V–nb) where nb is approximately the total volume occupied by the molecules themselves. Here, b is a constant. Having taken into account the corrections for pressure and volume, we can rewrite equation (5.17) as

$$\left(p + \frac{an^2}{V^2}\right)(V - nb) = nRT \quad (5.31)$$

Equation (5.31) is known as van der Waals equation. In this equation n is number of moles of the gas. Constants a and b are called van der Waals constants and their value depends on the characteristic of a gas. Value of

‘a’ is measure of magnitude of intermolecular attractive forces within the gas and is independent of temperature and pressure.

Also, at very low temperature, intermolecular forces become significant. As the molecules travel with low average speed, these can be captured by one another due to attractive forces. Real gases show ideal behaviour when conditions of temperature and pressure are such that the intermolecular forces are practically negligible. The real gases show ideal behaviour when pressure approaches zero.

The deviation from ideal behaviour can be measured in terms of **compressibility factor** Z, which is the ratio of product pV and nRT. Mathematically

$$Z = \frac{pV}{n\,RT} \quad (5.32)$$

For ideal gas Z = 1 at all temperatures and pressures because pV = n RT. The graph of Z vs p will be a straight line parallel to pressure axis (Fig. 5.12, page 152). For gases which deviate from ideality, value of Z deviates from unity. At very low pressures all gases shown have Z ≈1 and behave as ideal gas. At high pressure all the gases have Z > 1. These are more difficult to compress. At intermediate pressures, most gases have Z < 1. **Thus gases show ideal behaviour when the volume occupied is large so that the volume of the molecules can be neglected in comparison to it.** In other words, the behaviour of the gas becomes more ideal when pressure is very low. Upto what pressure a gas will follow the ideal gas law, depends upon nature of the gas and its temperature. The temperature at which a real gas obeys ideal gas law over an appreciable range of pressure is called **Boyle temperature or Boyle point.** Boyle point of a gas depends upon its nature. Above their Boyle point, real gases show positive deviations from ideality and Z values are greater than one. The forces of attraction between the

molecules are very feeble. Below Boyle temperature real gases first show decrease in Z value with increasing pressure, which reaches a minimum value. On further increase in pressure, the value of Z increases continuously. Above explanation shows that at low pressure and high temperature gases show ideal behaviour. These conditions are different for different gases.

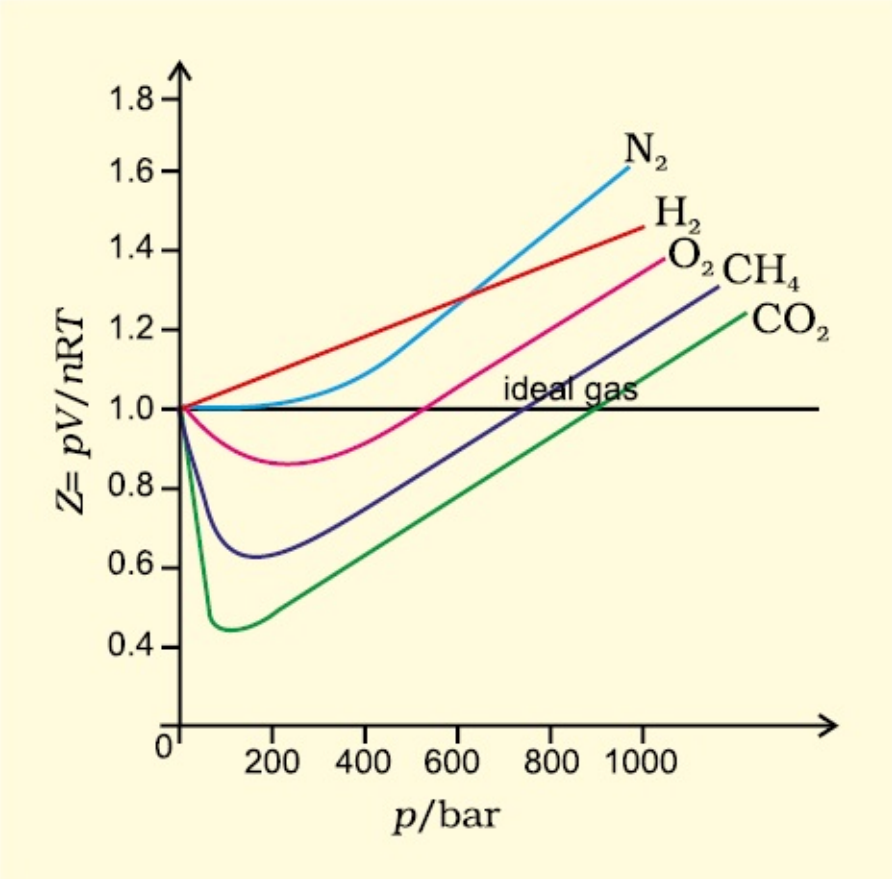


Fig. 5.12 Variation of compressibility factor for some gases

More insight is obtained in the significance of Z if we note the following derivation

$$Z = \frac{pV_{\text{real}}}{n\,RT} \quad (5.33)$$

If the gas shows ideal behaviour then

$V_{ideal} = \frac{n\,RT}{p}$. On putting this value of $\frac{nRT}{p}$ in equation (5.33) we have $Z = \frac{V_{real}}{V_{ideal}}$ (5.34)

From equation (5.34) we can see that compressibility factor is the ratio of actual molar volume of a gas to the molar volume of it, if it were an ideal gas at that temperature and pressure.

In the following sections we will see that it is not possible to distinguish between gaseous state and liquid state and that liquids may be considered as continuation of gas phase into a region of small volumes and very high molecular attraction. We will also see how we can use isotherms of gases for predicting the conditions for liquifaction of gases.

5.10 Liquifaction of Gases

First complete data on pressure-volume- temperature relations of a substance in both gaseous and liquid state was obtained by Thomas Andrews on Carbon dioxide. He plotted isotherms of carbon dioxide at various temperatures (Fig. 5.13). Later on it was found that real gases behave in the same manner as carbon dioxide. Andrews noticed that at high temperatures isotherms look like that of an ideal gas and the gas cannot be liquified even at very high pressure. As the temperature is lowered, shape of the curve changes and data show considerable deviation from ideal behaviour. At 30.98°C carbon dioxide remains gas upto 73 atmospheric pressure. (Point E in Fig. 5.13). At 73 atmospheric pressure, liquid carbon dioxide appears for the first time. The temperature 30.98°C is called **critical temperature (**TC**)** of carbon dioxide. This is the highest temperature at which liquid carbon dioxide is observed. Above this temperature it is gas. Volume of one mole of the gas at critical temperature is called **critical volume (**VC**)** and pressure at this temperature is called **critical pressure (**pC**)**. The critical

temperature, pressure and volume are called critical constants. Further increase in pressure simply compresses the liquid carbon dioxide and the curve represents the compressibility of the liquid. The steep line represents the isotherm of liquid. Even a slight compression results in steep rise in pressure indicating very low compressibility of the liquid. Below 30.98 °C, the behaviour of the gas on compression is quite different. At 21.5 °C, carbon dioxide remains as a gas only upto point B. At point B, liquid of a particular volume appears. Further compression does not change the pressure. Liquid and gaseous carbon dioxide coexist and further application of pressure results in the condensation of more gas until the point C is reached. At point C, all the gas has been condensed and further application of pressure merely compresses the liquid as shown by steep line. A slight compression from volume V_2 to V_3 results in steep rise in pressure from p_2 to p_3 (Fig. 5.13). Below 30.98 °C (critical temperature) each curve shows the similar trend. Only length of the horizontal line increases at lower temperatures. At critical point horizontal portion of the isotherm merges into one point. Thus we see that a point like A in the Fig. 5.13 represents gaseous state. A point like D represents liquid state and a point under the dome shaped area represents existence of liquid and gaseous carbon dioxide in equilibrium. All the gases upon compression at constant temperature (isothermal compression) show the same behaviour as shown by carbon dioxide. Also above discussion shows that gases should be cooled below their critical temperature for liquification. Critical temperature of a gas is highest temperature at which liquifaction of the gas first occurs. Liquifaction of so called permanent gases (i.e., gases which show continuous positive deviation in Z value) requires cooling as well as considerable compression. Compression brings the molecules in close vicinity and cooling slows down the movement of molecules therefore,

intermolecular interactions may hold the closely and slowly moving molecules together and the gas liquifies.

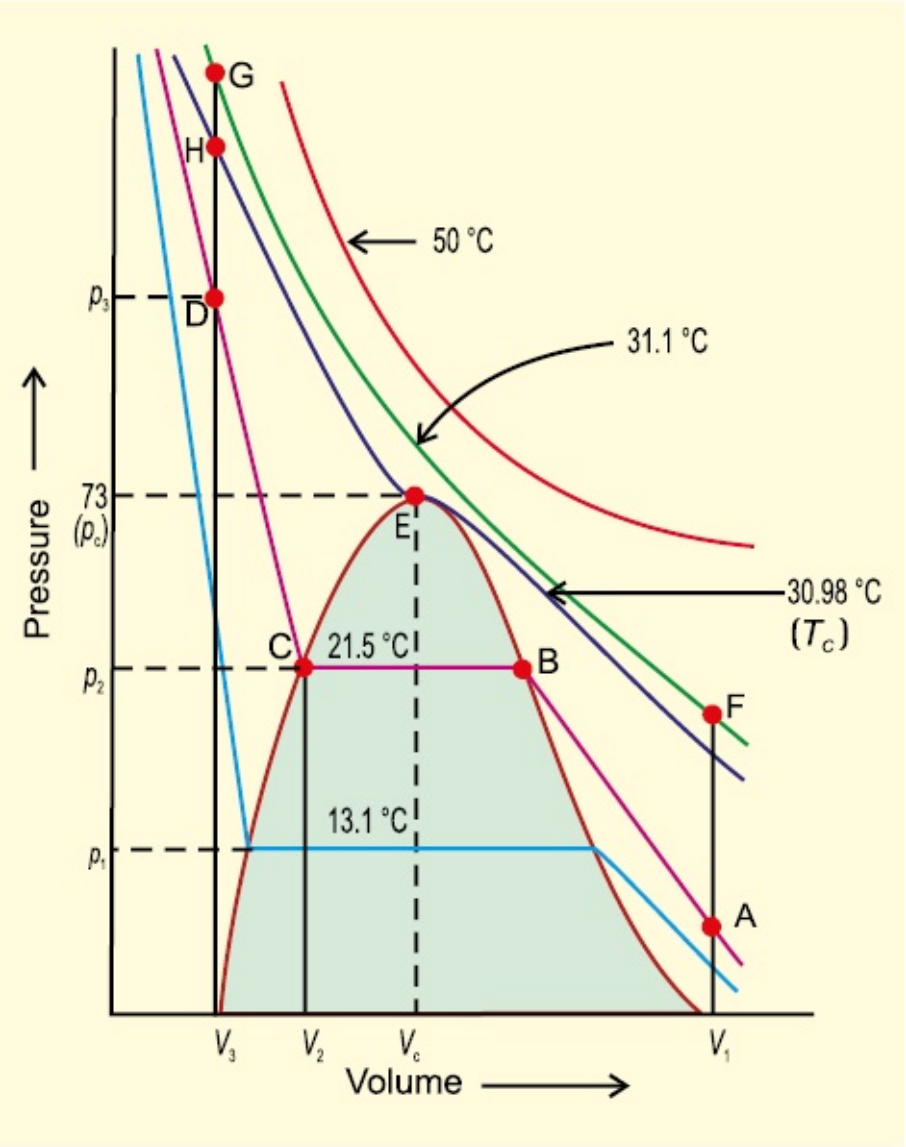


Fig. 5.13 Isotherms of carbon dioxide at various temperatures

It is possible to change a gas into liquid or a liquid into gas by a process in which always a single phase is present. For example in Fig. 5.13 we can move from point A to F vertically by increasing the temperature, then we can reach the point G by compressing the gas at the constant temperature along this isotherm (isotherm at 31.1°C). The

pressure will increase. Now we can move vertically down towards D by lowering the temperature. As soon as we cross the point H on the critical isotherm we get liquid. We end up with liquid but in this series of changes we do not pass through two-phase region. If process is carried out at the critical temperature, substance always remains in one phase.

Thus there is continuity between the gaseous and liquid state. The term fluid is used for either a liquid or a gas to recognise this continuity. Thus a liquid can be viewed as a very dense gas. Liquid and gas can be distinguished only when the fluid is below its critical temperature and its pressure and volume lie under the dome, since in that situation liquid and gas are in equilibrium and a surface separating the two phases is visible. In the absence of this surface there is no fundamental way of distinguishing between two states. At critical temperature, liquid passes into gaseous state imperceptibly and continuously; the surface separating two phases disappears (Section 5.11.1). A gas below the critical temperature can be liquified by applying pressure, and is called **vapour** of the substance. Carbon dioxide gas below its critical temperature is called carbon dioxide vapour. Critical constants for some common substances are given in Table 5.4.

Substance	T_c /K	p_c /bar	V_c/dm^3 mol^{-1}
H_2	33.2	12.97	0.0650
He	5.3	2.29	0.0577
N_2	126.0	33.9	0.0900
O_2	154.3	50.4	0.0744
CO_2	304.10	73.9	0.0956
H_2O	647.1	220.6	0.0450
NH_3	405.5	113.0	0.0723

Table 5.4 Critical Constants for Some Substances

Problem 5.5

Gases possess characteristic critical temperature which depends upon the magnitude of intermolecular forces between the gas particles. Critical temperatures of ammonia and carbon dioxide are 405.5 K and 304.10 K respectively. Which of these gases will liquify first when you start cooling from 500 K to their critical temperature ?

Solution

Ammonia will liquify first because its critical temperature will be reached first. Liquifaction of CO_2 will require more cooling.

5.11 Liquid State

Intermolecular forces are stronger in liquid state than in gaseous state. Molecules in liquids are so close that there is very little empty space between them and under normal conditions liquids are denser than gases.

Molecules of liquids are held together by attractive intermolecular forces. Liquids have definite volume because molecules do not separate from each other. However, molecules of liquids can move past one another freely, therefore, liquids can flow, can be poured and can assume the shape of the container in which these are stored. In the following sections we will look into some of the physical properties of the liquids such as vapour pressure, surface tension and viscosity.

5.11.1 Vapour Pressure

If an evacuated container is partially filled with a liquid, a portion of liquid evaporates to fill the remaining volume of the container with vapour. Initially the liquid evaporates and pressure exerted by vapours on the walls of the container (vapour pressure) increases. After some time it becomes constant, an equilibrium is established between liquid phase

and vapour phase. Vapour pressure at this stage is known as **equilibrium vapour pressure or saturated vapour pressure.**. Since process of vapourisation is temperature dependent; the temperature must be mentioned while reporting the vapour pressure of a liquid.

When a liquid is heated in an open vessel, the liquid vapourises from the surface. At the temperature at which vapour pressure of the liquid becomes equal to the external pressure, vapourisation can occur throughout the bulk of the liquid and vapours expand freely into the surroundings. The condition of free vapourisation throughout the liquid is called boiling. The temperature at which vapour pressure of liquid is equal to the external pressure is called boiling temperature at that pressure. Vapour pressure of some common liquids at various temperatures is given in (Fig. 5.14, page 155). At 1 atm pressure boiling temperature is called **normal boiling point**. If pressure is 1 bar then the boiling point is called **standard boiling point** of the liquid. Standard boiling point of the liquid is slightly lower than the normal boiling point because 1 bar pressure is slightly less than 1 atm pressure. The normal boiling point of water is 100 °C (373 K), its standard boiling point is 99.6 °C (372.6 K).

At high altitudes atmospheric pressure is low. Therefore liquids at high altitudes boil at lower temperatures in comparison to that at sea level. Since water boils at low temperature on hills, the pressure cooker is used for cooking food. In hospitals surgical instruments are sterilized in autoclaves in which boiling point of water is increased by increasing the pressure above the atmospheric pressure by using a weight covering the vent.

Boiling does not occur when liquid is heated in a closed vessel. On heating continuously vapour pressure increases. At first a clear boundary is visible between liquid and vapour phase because liquid is more dense than vapour. As the temperature increases more and more molecules go

to vapour phase and density of vapours rises. At the same time liquid becomes less dense. It expands because molecules move apart. When density of liquid and vapours becomes the same; the clear boundary between liquid and vapours disappears. This temperature is called **critical temperature** about which we have already discussed in section 5.10.

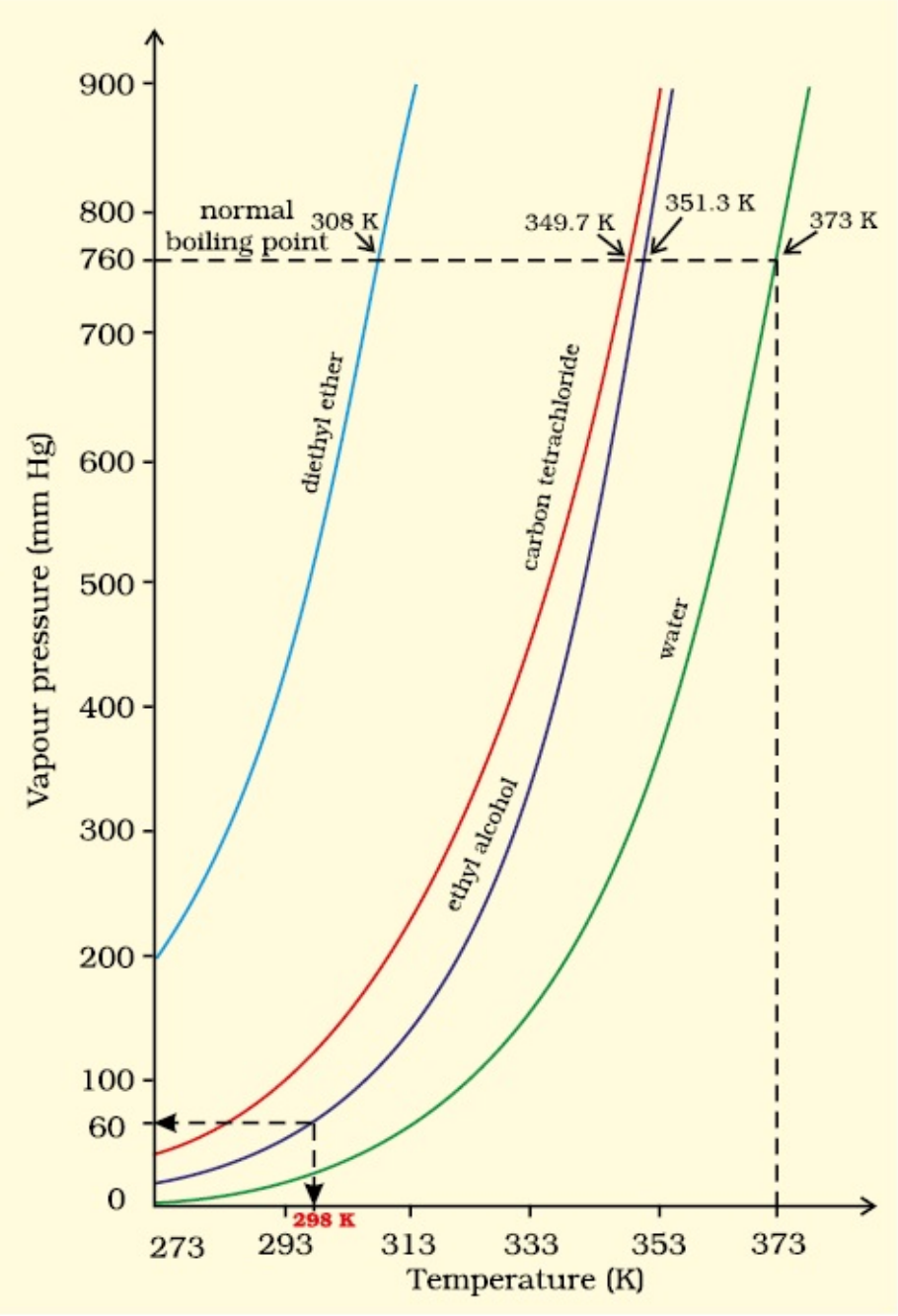


Fig. 5.14 Vapour pressure vs temperature curve of some common liquids.

5.11.2 Surface Tension

It is well known fact that liquids assume the shape of the container. Why is it then small drops of mercury form spherical bead instead of spreading on the surface. Why do particles of soil at the bottom of river remain separated but they stick together when taken out ? Why does a liquid rise (or fall) in a thin capillary as soon as the capillary touches the surface of the liquid ? All these phenomena are caused due to the characteristic property of liquids, called **surface tension**. A molecule in the bulk of liquid experiences equal intermolecular forces from all sides. The molecule, therefore does not experience any net force. But for the molecule on the surface of liquid, net attractive force is towards the interior of the liquid (Fig. 5.15), due to the molecules below it. Since there are no molecules above it.

Liquids tend to minimize their surface area. The molecules on the surface experience a net downward force and have more energy than the molecules in the bulk, which do not experience any net force. Therefore, liquids tend to have minimum number of molecules at their surface. If surface of the liquid is increased by pulling a molecule from the bulk, attractive forces will have to be overcome. This will require expenditure of energy. The energy required to increase the surface area of the liquid by one unit is defined as surface energy. Its dimensions are J m^{-2}. Surface tension is defined as the force acting per unit length perpendicular to the line drawn on the surface of liquid. It is denoted by Greek letter γ (Gamma). It has dimensions of kg s^{-2} and in SI unit it is expressed as N m^{-1}. The lowest energy state of the liquid will be when surface area is minimum. Spherical shape satisfies this condition, that is why mercury drops are spherical in shape. This is the reason that sharp glass edges are heated for making them smooth. On heating, the glass melts and the surface of the liquid tends to take the rounded shape at the edges, which

makes the edges smooth. This is called fire polishing of glass.

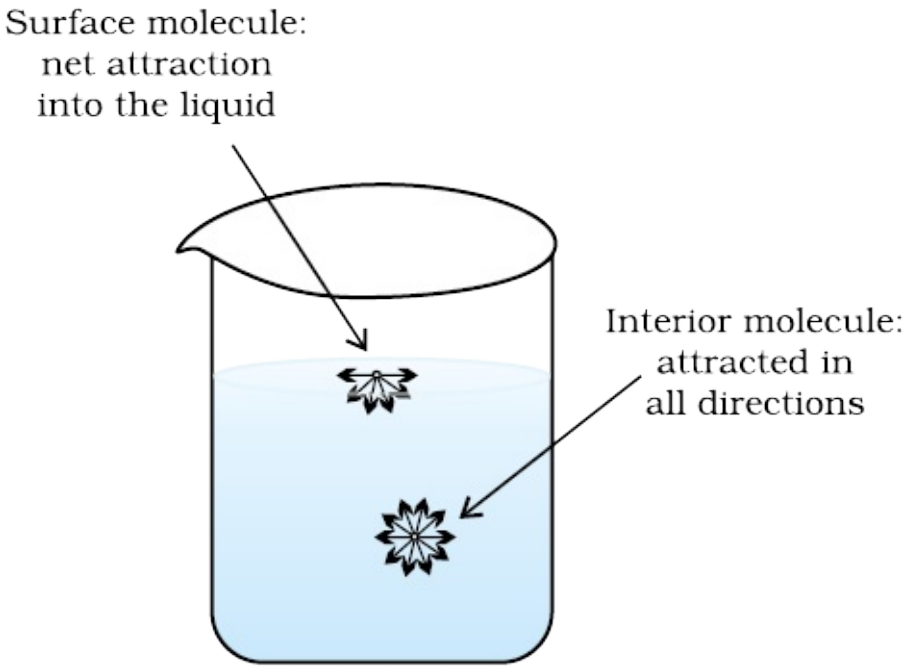


Fig. 5.15 Forces acting on a molecule on liquid surface and on a molecule inside the liquid

Liquid tends to rise (or fall) in the capillary because of surface tension. Liquids wet the things because they spread across their surfaces as thin film. Moist soil grains are pulled together because surface area of thin film of water is reduced. It is surface tension which gives stretching property to the surface of a liquid. On flat surface, droplets are slightly flattened by the effect of gravity; but in the gravity free environments drops are perfectly spherical.

The magnitude of surface tension of a liquid depends on the attractive forces between the molecules. When the attractive forces are large, the surface tension is large. Increase in temperature increases the kinetic energy of the molecules and effectiveness of intermolecular attraction decreases, so surface tension decreases as the temperature is raised.

5.11.3 Viscosity

It is one of the characteristic properties of liquids. Viscosity is a measure of resistance to flow which arises due to the internal friction between layers of fluid as they slip past one another while liquid flows. Strong

intermolecular forces between molecules hold them together and resist movement of layers past one another.

When a liquid flows over a fixed surface, the layer of molecules in the immediate contact of surface is stationary. The velocity of upper layers increases as the distance of layers from the fixed layer increases. This type of flow in which there is a regular gradation of velocity in passing from one layer to the next is called **laminar flow**. If we choose any layer in the flowing liquid (Fig.5.16), the layer above it accelerates its flow and the layer below this retards its flow.

If the velocity of the layer at a distance dz is changed by a value du then velocity gradient is given by the amount . $\frac{du}{dz}$ A force is required to maintain the flow of layers. This force is proportional to the area of contact of layers and velocity gradient i.e.

$$F \propto A \text{ (A is the area of contact)}$$

$$F \propto \mathrm{A}.\frac{du}{dz} \text{ (where, } \frac{du}{dz} \text{ is velocity gradient;}$$

the change in velocity with distance)

$$F \propto \mathrm{A}.\frac{du}{dz}$$

$$\Rightarrow F = \eta \mathrm{A}\frac{du}{dz}$$

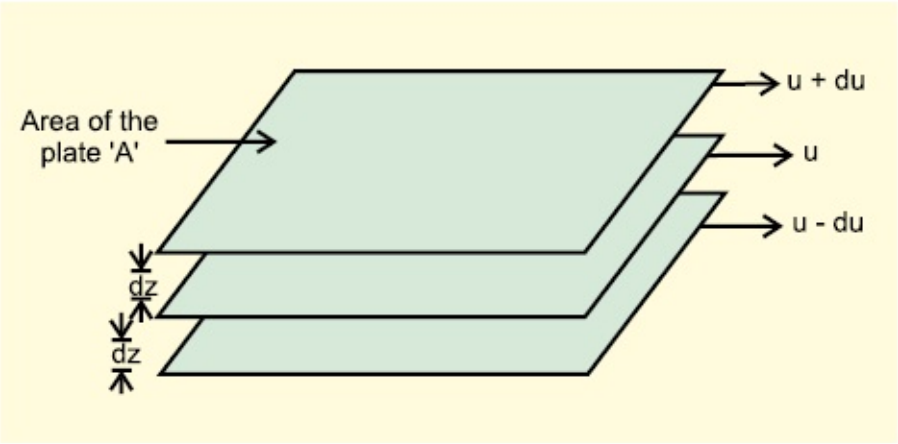


Fig. 5.16 Gradation of velocity in the laminar flow

'η'' is proportionality constant and is called **coefficient of viscosity**. Viscosity coefficient is the force when velocity gradient is unity and the area of contact is unit area. Thus 'η' is measure of viscosity. SI unit of viscosity coefficient is 1 newton second per square metre (N s m–2) = pascal second (Pa s = 1kg m–1s–1). In cgs system the unit of coefficient of viscosity is poise (named after great scientist Jean Louise Poiseuille).

1 poise = 1 g cm–1s–1 = 10–1kg m–1s–1

Greater the viscosity, the more slowly the liquid flows. Hydrogen bonding and van der Waals forces are strong enough to cause high viscosity. Glass is an extremely viscous liquid. It is so viscous that many of its properties resemble solids.

Viscosity of liquids decreases as the temperature rises because at high temperature molecules have high kinetic energy and can overcome the intermolecular forces to slip past one another between the layers.

Summary

Intermolecular forces operate between the particles of matter. These forces differ from pure electrostatic forces that exist between two oppositely charged ions. Also, these do not include forces that hold atoms of a covalent molecule together through covalent bond. Competition between thermal energy and intermolecular interactions determines the state of

matter. “Bulk” properties of matter such as behaviour of gases, characteristics of solids and liquids and change of state depend upon energy of constituent particles and the type of interaction between them. Chemical properties of a substance do not change with change of state, but the reactivity depends upon the physical state.

Forces of interaction between gas molecules are negligible and are almost independent of their chemical nature. Interdependence of some observable properties namely pressure, volume, temperature and mass leads to different gas laws obtained from experimental studies on gases. Boyle’s law states that under isothermal condition, pressure of a fixed amount of a gas is inversely proportional to its volume. Charles’ law is a relationship between volume and absolute temperature under isobaric condition. It states that volume of a fixed amount of gas is directly proportional to its absolute temperature $(V \propto T)$. If state of a gas is represented by p1, V1 and T1 and it changes to state at p2, V2 and T2, then relationship between these two states is given by combined gas law according to which $\frac{p_1 V_1}{T_1} = \frac{p_2 V_2}{T_2}$. Any one of the variables of this gas can be found out if other five variables are known. Avogadro law states that equal volumes of all gases under same conditions of temperature and pressure contain equal number of molecules. Dalton’s law of partial pressure states that total pressure exerted by a mixture of non-reacting gases is equal to the sum of partial pressures exerted by them. Thus p = p1+p2+p3+ ... . Relationship between pressure, volume, temperature and number of moles of a gas describes its state and is called equation of state of the gas. Equation of state for ideal gas is pV=nRT, where R is a gas constant and its value depends upon units chosen for pressure, volume and temperature.

At high pressure and low temperature intermolecular forces start operating strongly between the molecules of gases because they come close to each other. Under suitable temperature and pressure conditions gases can be liquified. Liquids may be considered as continuation of gas phase into a region of small volume and very strong molecular attractions. Some properties of liquids e.g., surface tension and viscosity are due to strong intermolecular attractive forces.

Exercises

5.1 What will be the minimum pressure required to compress 500 dm3 of air at 1 bar to 200 dm3 at 30°C?

5.2 A vessel of 120 mL capacity contains a certain amount of gas at 35 °C and 1.2 bar pressure. The gas is transferred to another vessel of volume 180 mL at 35 °C. What would be its pressure?

5.3 Using the equation of state pV=nRT; show that at a given temperature density of a gas is proportional to gas pressure p.

5.4 At 0°C, the density of a certain oxide of a gas at 2 bar is same as that of dinitrogen at 5 bar. What is the molecular mass of the oxide?

5.5 Pressure of 1 g of an ideal gas A at 27 °C is found to be 2 bar. When 2 g of another ideal gas B is introduced in the same flask at same temperature the pressure becomes 3 bar. Find a relationship between their molecular masses.

5.6 The drain cleaner, Drainex contains small bits of aluminum which react with caustic soda to produce dihydrogen. What volume of dihydrogen at 20 °C and one bar will be released when 0.15g of aluminum reacts?

5.7 What will be the pressure exerted by a mixture of 3.2 g of methane and 4.4 g of carbon dioxide contained in a 9 dm3 flask at 27 °C ?

5.8 What will be the pressure of the gaseous mixture when 0.5 L of H2 at 0.8 bar and 2.0 L of dioxygen at 0.7 bar are introduced in a 1L vessel at 27°C?

5.9 Density of a gas is found to be 5.46 g/dm3 at 27 °C at 2 bar pressure. What will be its density at STP?

5.10 34.05 mL of phosphorus vapour weighs 0.0625 g at 546 °C and 0.1 bar pressure. What is the molar mass of phosphorus?

5.11 A student forgot to add the reaction mixture to the round bottomed

flask at 27 °C but instead he/she placed the flask on the flame. After a lapse of time, he realized his mistake, and using a pyrometer he found the temperature of the flask was 477 °C. What fraction of air would have been expelled out?

5.12 Calculate the temperature of 4.0 mol of a gas occupying 5 dm3 at 3.32 bar.

(R = 0.083 bar dm3 K–1 mol–1).

5.13 Calculate the total number of electrons present in 1.4 g of dinitrogen gas.

5.14 How much time would it take to distribute one Avogadro number of wheat grains, if 1010 grains are distributed each second ?

5.15 Calculate the total pressure in a mixture of 8 g of dioxygen and 4 g of dihydrogen confined in a vessel of 1 dm3 at 27°C. R = 0.083 bar dm3 K–1 mol–1.

5.16 Pay load is defined as the difference between the mass of displaced air and the mass of the balloon. Calculate the pay load when a balloon of radius 10 m, mass 100 kg is filled with helium at 1.66 bar at 27°C. (Density of air = 1.2 kg m–3 and R = 0.083 bar dm3 K–1 mol–1).

5.17 Calculate the volume occupied by 8.8 g of CO2 at 31.1°C and 1 bar pressure.

R = 0.083 bar L K–1 mol–1.

5.18 2.9 g of a gas at 95 °C occupied the same volume as 0.184 g of dihydrogen at 17 °C, at the same pressure. What is the molar mass of the gas?

5.19 A mixture of dihydrogen and dioxygen at one bar pressure contains 20% by weight of dihydrogen. Calculate the partial pressure of dihydrogen.

5.20 What would be the SI unit for the quantity pV 2T 2/n ?

5.21 In terms of Charles' law explain why –273 °C is the lowest possible temperature.

5.22 Critical temperature for carbon dioxide and methane are 31.1 °C and –81.9 °C respectively. Which of these has stronger intermolecular forces and why?

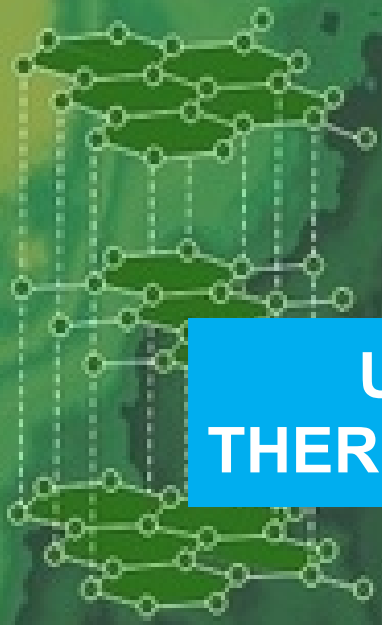
5.23 Explain the physical significance of van der Waals parameters.

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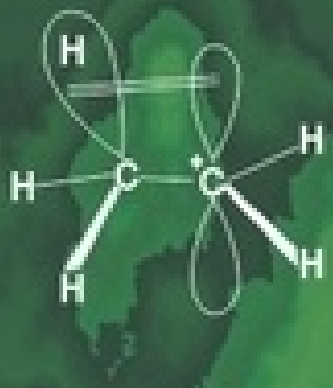
Textbook for Class XI



Unit 6
THERMODYNAMICS

Chemistry

Part I



11082CH06

Unit 6

THERMODYNAMICS

Objectives

After studying this Unit, you will be able to

- explain the terms : system and surroundings;
- discriminate between close, open and isolated systems;
- explain internal energy, work and heat;
- state first law of thermodynamics and express it mathematically;
- calculate energy changes as work and heat contributions in chemical systems;
- explain state functions: U, H.
- correlate ΔU and ΔH;
- measure experimentally ΔU and ΔH;
- define standard states for ΔH;
- calculate enthalpy changes for various types of reactions;
- state and apply Hess's law of constant heat summation;
- differentiate between extensive and intensive properties;
- define spontaneous and non-spontaneous processes;
- explain entropy as a thermodynamic state function and apply it for spontaneity;
- explain Gibbs energy change (ΔG); and
- establish relationship between ΔG and spontaneity, ΔG and equilibrium constant.

It is the only physical theory of universal content concerning which I am convinced that, within the framework of the applicability of its basic concepts, it will never be overthrown.

Albert Einstein

Chemical energy stored by molecules can be released as heat during chemical reactions when a fuel like methane, cooking gas or coal burns in air. The chemical energy may also be used to do mechanical work when a fuel burns in an engine or to provide electrical energy through a galvanic cell like dry cell. Thus, various forms of energy are interrelated and under certain conditions, these may be transformed from one form into another. The study of these energy transformations forms the subject matter of thermodynamics. The laws of thermodynamics deal with energy changes of macroscopic systems involving a large number of molecules rather than microscopic systems containing a few molecules. Thermodynamics is not concerned about how and at what rate these energy transformations are carried out, but is based on initial and final states of a system undergoing the change. Laws of thermodynamics apply only when a system is in equilibrium or moves from one equilibrium state to another equilibrium state. Macroscopic properties like pressure and temperature do not change with time for a system in equilibrium state. In this unit, we would like to answer some of the important questions through thermodynamics, like:

How do we determine the energy changes involved in a chemical reaction/process? Will it occur or not?

What drives a chemical reaction/process?

To what extent do the chemical reactions proceed?

6.1 Thermodynamic terms

We are interested in chemical reactions and the energy changes accompanying them. For this we need to know certain thermodynamic terms. These are discussed below.

6.1.1 The System and the Surroundings

A **system** in thermodynamics refers to that part of universe in which observations are made and remaining universe constitutes the **surroundings.** The surroundings include everything other than the system. System and the surroundings together constitute the universe .

The universe = The system + The surroundings

However, the entire universe other than the system is not affected by the changes taking place in the system. Therefore, for all practical purposes, the surroundings are that portion of the remaining universe which can interact with the system. Usually, the region of space in the neighbourhood of the system constitutes its surroundings.

For example, if we are studying the reaction between two substances A and B kept in a beaker, the beaker containing the reaction mixture is the system and the room where the beaker is kept is the surroundings (Fig. 6.1).

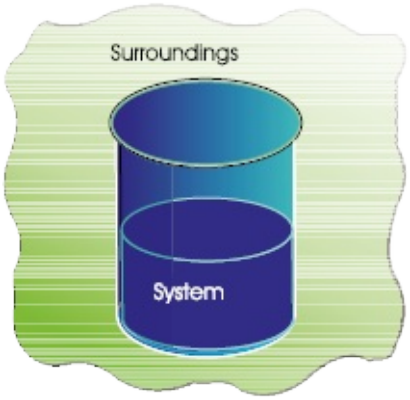


Fig. 6.1 System and the surroundings

Note that the system may be defined by physical boundaries, like beaker or test tube, or the system may simply be defined by a set of Cartesian coordinates specifying a particular volume in space. It is necessary to

think of the system as separated from the surroundings by some sort of wall which may be real or imaginary. The wall that separates the system from the surroundings is called **boundary**. This is designed to allow us to control and keep track of all movements of matter and energy in or out of the system.

6.1.2 Types of the System

We, further classify the systems according to the movements of matter and energy in or out of the system.

1. Open System

In an open system, there is exchange of energy and matter between system and surroundings [Fig. 6.2 (a)]. The presence of reactants in an open beaker is an example of an open system*. Here the boundary is an imaginary surface enclosing the beaker and reactants.

2. Closed System

In a closed system, there is no exchange of matter, but exchange of energy is possible between system and the surroundings
[Fig. 6.2 (b)]. The presence of reactants in a closed vessel made of conducting material e.g., copper or steel is an example of a closed system.

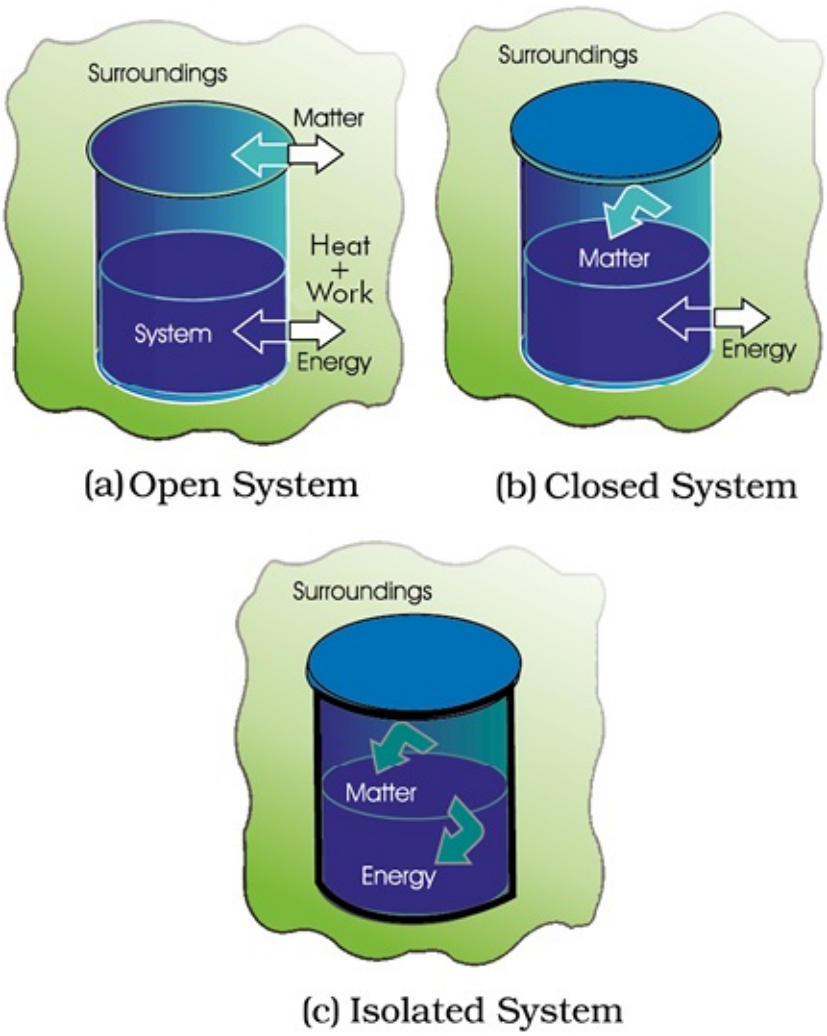


Fig. 6.2 Open, closed and isolated systems.

* *We could have chosen only the reactants as system then walls of the beakers will act as boundary.*

3. Isolated System

In an isolated system, there is no exchange of energy or matter between the system and the surroundings [Fig. 6.2 (c)]. The presence of reactants in a thermos flask or any other closed insulated vessel is an example of an isolated system.

6.1.3 The State of the System

The system must be described in order to make any useful calculations by specifying quantitatively each of the properties such as its pressure

(p), volume (V), and temperature (T) as well as the composition of the system. We need to describe the system by specifying it before and after the change. You would recall from your Physics course that the state of a system in mechanics is completely specified at a given instant of time, by the position and velocity of each mass point of the system. In thermodynamics, a different and much simpler concept of the state of a system is introduced. It does not need detailed knowledge of motion of each particle because, we deal with average measurable properties of the system. We specify the state of the system by state functions or state variables.

The **state** of a thermodynamic system is described by its measurable or macroscopic (bulk) properties. We can describe the state of a gas by quoting its pressure (p), volume (V), temperature (T), amount (n) etc. Variables like p, V, T are called **state variables** or **state functions** because their values depend only on the state of the system and not on how it is reached. In order to completely define the state of a system it is not necessary to define all the properties of the system; as only a certain number of properties can be varied independently. This number depends on the nature of the system. Once these minimum number of macroscopic properties are fixed, others automatically have definite values.

The state of the surroundings can never be completely specified; fortunately it is not necessary to do so.

6.1.4 The Internal Energy as a State Function

When we talk about our chemical system losing or gaining energy, we need to introduce a quantity which represents the total energy of the system. It may be chemical, electrical, mechanical or any other type of energy you may think of, the sum of all these is the energy of the system. In thermodynamics, we call it the internal energy, U of the system, which may change, when

• heat passes into or out of the system,
• work is done on or by the system,
• matter enters or leaves the system.

These systems are classified accordingly as you have already studied in section 6.1.2.

(a) Work

Let us first examine a change in internal energy by doing work. We take a system containing some quantity of water in a thermos flask or in an insulated beaker. This would not allow exchange of heat between the system and surroundings through its boundary and we call this type of system as **adiabatic**. The manner in which the state of such a system may be changed will be called adiabatic process. Adiabatic process is a process in which there is no transfer of heat between the system and surroundings. Here, the wall separating the system and the surroundings is called the adiabatic wall (Fig 6.3).

Let us bring the change in the internal energy of the system by doing some work on it. Let us call the initial state of the system as state A and its temperature as T_A. Let the internal energy of the system in state A be called U_A. We can change the state of the system in two different ways.

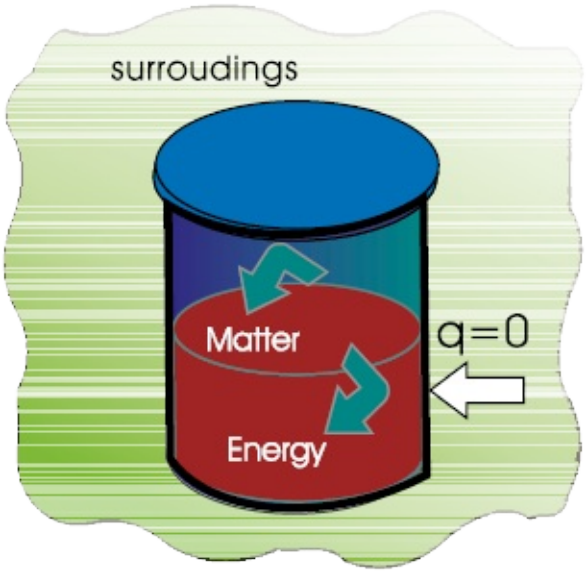


Fig. 6.3 An adiabatic system which does not permit the transfer of heat through its boundary.

One way: We do some mechanical work, say 1 kJ, by rotating a set of small paddles and thereby churning water. Let the new state be called B state and its temperature, as T_B. It is found that $T_B > T_A$ and the change in temperature, $\Delta T = T_B - T_A$. Let the internal energy of the system in state B be U_B and the change in internal energy, $\Delta U = U_B - U_A$.

Second way: We now do an equal amount (i.e., 1kJ) electrical work with the help of an immersion rod and note down the temperature change. We find that the change in temperature is same as in the earlier case, say, $T_B - T_A$.

In fact, the experiments in the above manner were done by J. P. Joule between 1840–50 and he was able to show that a given amount of work done on the system, no matter how it was done (irrespective of path) produced the same change of state, as measured by the change in the temperature of the system.

So, it seems appropriate to define a quantity, the internal energy U, whose value is characteristic of the state of a system, whereby the adiabatic work, w_{ad} required to bring about a change of state is equal to the difference between the value of U in one state and that in another state, ΔU i.e.,

$$\Delta U = U_2 - U_1 = w_{ad}$$

Therefore, internal energy, U, of the system is a state function.

By conventions of IUPAC in chemical thermodynamics. The positive sign expresses that w_{ad} is positive when work is done **on** the system and the internal energy of system increases. Similarly, if the work is done **by** the system,w_{ad} will be negative because internal energy of the system decreases.

Can you name some other familiar state functions? Some of other

familiar state functions are V, p, and T. For example, if we bring a change in temperature of the system from 25°C to 35°C, the change in temperature is 35°C–25°C = +10°C, whether we go straight up to 35°C or we cool the system for a few degrees, then take the system to the final temperature. Thus, T is a state function and the change in temperature is independent of the route taken. Volume of water in a pond, for example, is a state function, because change in volume of its water is independent of the route by which water is filled in the pond, either by rain or by tubewell or by both.

(b) Heat

We can also change the internal energy of a system by transfer of heat from the surroundings to the system or vice-versa without expenditure of work. This exchange of energy, which is a result of temperature difference is called heat, q. Let us consider bringing about the same change in temperature (the same initial and final states as before in section 6.1.4 (a) by transfer of heat through thermally conducting walls instead of adiabatic walls (Fig. 6.4).

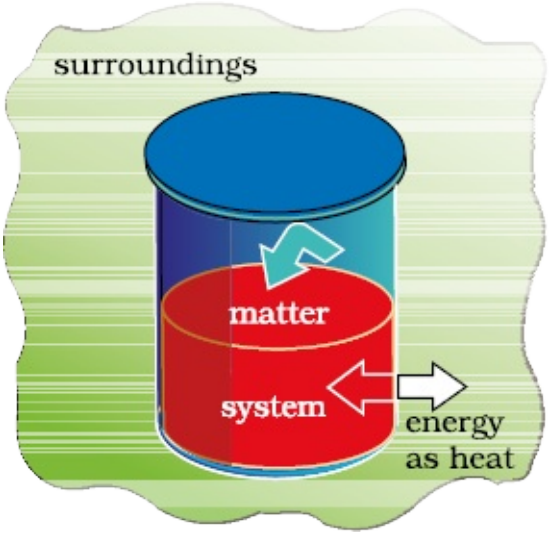


Fig. 6.4 A system which allows heat transfer through its boundary.

We take water at temperature, T_A in a container having thermally conducting walls, say made up of copper and enclose it in a huge heat

reservoir at temperature, T_B. The heat absorbed by the system (water), q can be measured in terms of temperature difference , $T_B - T_A$. In this case change in internal energy, $\Delta U = q$, when no work is done at constant volume.

By conventions of IUPAC in chemical thermodynamics. The q is positive, when heat is transferred from the surroundings to the system and the internal energy of the system increases and q is negative when heat is transferred from system to the surroundings resulting in decrease of the internal energy of the system..

** Earlier negative sign was assigned when the work is done on the system and positive sign when the work is done by the system. This is still followed in physics books, although IUPAC has recommended the use of new sign convention.*

(c) The general case

Let us consider the general case in which a change of state is brought about both by doing work and by transfer of heat. We write change in internal energy for this case as:

$\Delta U = q + w$ (6.1)

For a given change in state, q and w can vary depending on how the change is carried out. However, $q + w = \Delta U$ will depend only on initial and final state. It will be independent of the way the change is carried out. If there is no transfer of energy as heat or as work (isolated system) i.e., if w = 0 and q = 0, then

$\Delta U = 0$.

The equation 6.1 i.e., $\Delta U = q + w$ is mathematical statement of the **first law of thermodynamics**, which states that

The energy of an isolated system is constant.

It is commonly stated as the law of conservation of energy i.e., energy

can neither be created nor be destroyed.

Note: There is considerable difference between the character of the thermodynamic property energy and that of a mechanical property such as volume. We can specify an unambiguous (absolute) value for volume of a system in a particular state, but not the absolute value of the internal energy. However, we can measure only the changes in the internal energy, ΔU of the system.

Problem 6.1

Express the change in internal energy of a system when

(i) No heat is absorbed by the system from the surroundings, but work (w) is done on the system. What type of wall does the system have ?

(ii) No work is done on the system, but q amount of heat is taken out from the system and given to the surroundings. What type of wall does the system have?

(iii) w amount of work is done by the system and q amount of heat is supplied to the system. What type of system would it be?

Solution

(i) $\Delta U = w_{ad}$, wall is adiabatic

(ii) $\Delta U = -q$, thermally conducting walls

(iii) $\Delta U = q - w$, closed system.

6.2 Applications

Many chemical reactions involve the generation of gases capable of doing mechanical work or the generation of heat. It is important for us to quantify these changes and relate them to the changes in the internal energy. Let us see how!

6.2.1 Work

First of all, let us concentrate on the nature of work a system can do. We

will consider only mechanical work i.e., pressure-volume work.

For understanding pressure-volume work, let us consider a cylinder which contains one mole of an ideal gas fitted with a frictionless piston. Total volume of the gas is V_i and pressure of the gas inside is p. If external pressure is p_{ex} which is greater than p, piston is moved inward till the pressure inside becomes equal to p_{ex}. Let this change be achieved in a single step and the final volume be V_f . During this compression, suppose piston moves a distance, l and is cross-sectional area of the piston is A

[Fig. 6.5(a)].

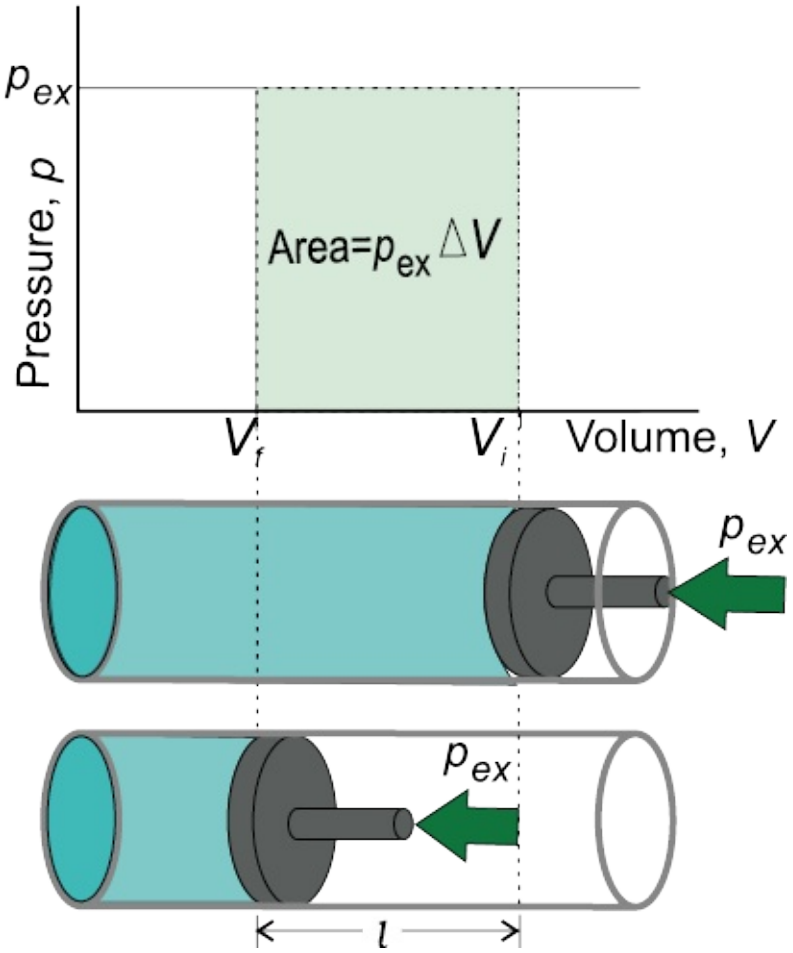


Fig. 6.5(a) Work done on an ideal gas in a cylinder when it is compressed by a constant external pressure, pex

(in single step) is equal to the shaded area.

then, volume change = l × A = $\Delta V = (V_f - V_i)$

We also know, $\text{pressure} = \frac{\text{force}}{\text{area}}$

Therefore, force on the piston = p_{ex} . A

If w is the work done on the system by movement of the piston then
w = force × distance = p_{ex} . A .l

= p_{ex} . $(-\Delta V) = - p_{ex} \Delta V = - p_{ex} (V_f - V_i)$ (6.2)

The negative sign of this expression is required to obtain conventional sign for w, which will be positive. It indicates that in case of compression work is done on the system. Here $(V_f - V_i)$ will be negative and negative multiplied by negative will be positive. Hence the sign obtained for the work will be positive.

If the pressure is not constant at every stage of compression, but changes in number of finite steps, work done on the gas will be summed over all the steps and will be equal to $-\sum p\Delta V$ [Fig. 6.5 (b)]

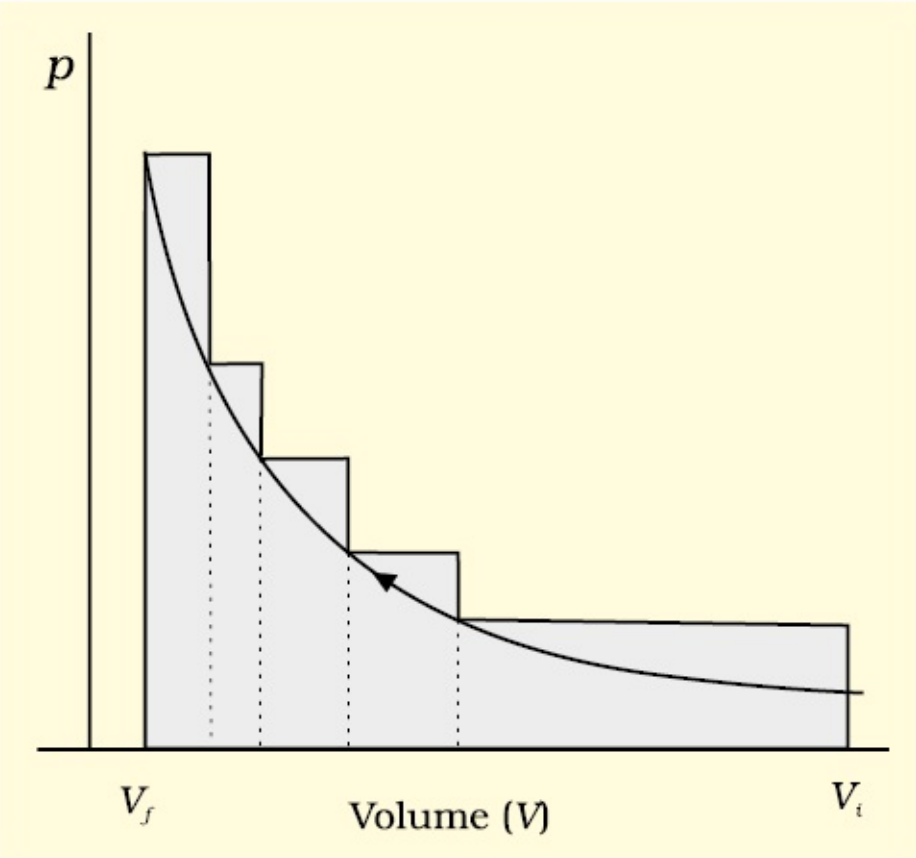


Fig. 6.5 (b) pV-plot when pressure is not constant and changes in finite steps during compression from initial volume, V_i to final volume, V_f. Work done on the gas is represented by the shaded area.

If the pressure is not constant but changes during the process such that it is always infinitesimally greater than the pressure of the gas, then, at each stage of compression, the volume decreases by an infinitesimal amount, dV. In such a case we can calculate the work done on the gas by the relation

$$w = -\int_{V_i}^{V_f} p_{ex} dV \qquad (6.3)$$

Here, p_{ex} at each stage is equal to (p_{in} + dp) in case of compression [Fig. 6.5(c)]. In an expansion process under similar conditions, the external pressure is always less than the pressure of the system i.e., p_{ex} = (p_{in}– dp). In general case we can write, p_{ex} = (p_{in} + dp). Such processes are

called reversible processes.

A process or change is said to be reversible, if a change is brought out in such a way that the process could, at any moment, be reversed by an infinitesimal change. A reversible process proceeds infinitely slowly by a series of equilibrium states such that system and the surroundings are always in near equilibrium with each other. Processes other than reversible processes are known as irreversible processes.

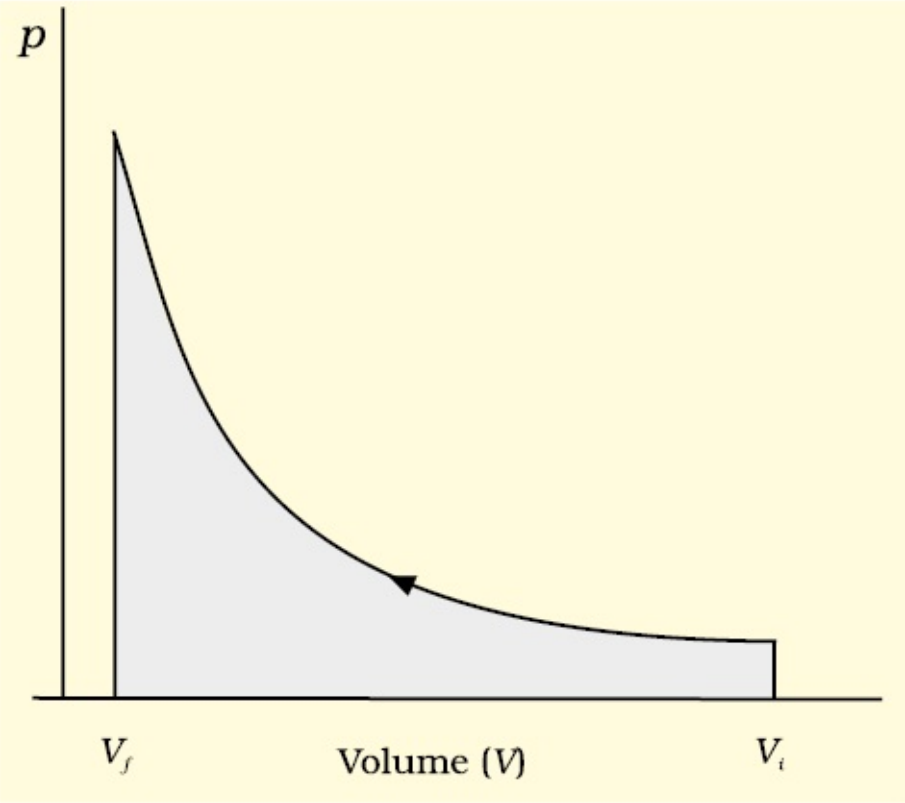


Fig. 6.5 (c) pV-plot when pressure is not constant and changes in infinite steps (reversible conditions) during compression from initial volume, Vi to final volume, Vf . Work done on the gas is represented by the shaded area.

In chemistry, we face problems that can be solved if we relate the work term to the **internal pressure of the system.** We can relate work to internal pressure of the system under **reversible conditions** by writing equation 6.3 as follows:

$$w_{rev} = -\int_{V_i}^{V_f} p_{ex} dV = -\int_{V_i}^{V_f} (p_{in} \pm dp)\, dV$$

Since $dp \times dV$ is very small we can write

$$w_{rev} = -\int_{V_i}^{V_f} p_{in} dV \qquad (6.4)$$

Now, the pressure of the gas (p_{in} which we can write as p now) can be expressed in terms of its volume through gas equation. For n mol of an ideal gas i.e., pV =nRT

$$\Rightarrow p = \frac{nRT}{V}$$

Therefore, at constant temperature (isothermal process),

$$w_{rev} = -\int_{V_i}^{V_f} nRT \frac{dV}{V} = -nRT \ln \frac{V_f}{V_i}$$

$$= -2.303\ nRT \log \frac{V_f}{V_i} \qquad (6.5)$$

Free expansion: Expansion of a gas in vacuum (p_{ex} = 0) is called free expansion. No work is done during free expansion of an ideal gas whether the process is reversible or irreversible (equation 6.2 and 6.3).

Now, we can write equation 6.1 in number of ways depending on the type of processes.

Let us substitute w = – $p_{ex}\Delta V$ (eq. 6.2) in equation 6.1, and we get

$$\Delta U = q - p_{ex}\Delta V$$

If a process is carried out at constant volume (ΔV = 0), then

$\Delta U = q_V$

the subscript V in q_V denotes that heat is supplied at constant volume.

Isothermal and free expansion of an ideal gas

For isothermal (T = constant) expansion of an ideal gas into vacuum ; w = 0 since p_{ex} = 0. Also, Joule determined experimentally that

q = 0; therefore, $\Delta U = 0$

Equation 6.1, $\Delta U = q + w$ can be expressed for isothermal irreversible and reversible changes as follows:

1. For isothermal irreversible change

$q = - w = p_{ex} (V_f - V_i)$

2. For isothermal reversible change

$q = - w = nRT \ln \frac{V_f}{V_i}$

$= 2.303\ nRT \log \frac{V_f}{V_i}$

3. For adiabatic change, q = 0,

$\Delta U = w_{ad}$

Problem 6.2

Two litres of an ideal gas at a pressure of 10 atm expands isothermally at 25 °C into a vacuum until its total volume is 10 litres. How much heat is absorbed and how much work is done in the expansion ?

Solution

We have $q = - w = p_{ex} (10 - 2) = 0(8) = 0$

No work is done; no heat is absorbed.

Problem 6.3

Consider the same expansion, but this time against a constant external pressure of 1 atm.

Solution

We have $q = - w = p_{ex} (8) = 8$ litre-atm

Problem 6.4

Consider the expansion given in problem 6.2, for 1 mol of an ideal gas conducted reversibly.

Solution

We have q = – w = 2.303 nRT $\log \frac{V_f}{V_s}$

= 2.303 × 1 × 0.8206 × 298 × log $\frac{10}{2}$

= 2.303 x 0.8206 x 298 x log 5

= 2.303 x 0.8206 x 298 x 0.6990

= 393.66 L atm

6.2.2 Enthalpy, H

(a) A Useful New State Function

We know that the heat absorbed at constant volume is equal to change in the internal energy i.e., $\Delta U = q_V$. But most of chemical reactions are carried out not at constant volume, but in flasks or test tubes under constant atmospheric pressure. We need to define another state function which may be suitable under these conditions.

We may write equation (6.1) as

$\Delta U = q_p - p\Delta V$ at constant pressure, where q_p is heat absorbed by the system and $-p\Delta V$ represent expansion work done by the system.

Let us represent the initial state by subscript 1 and final state by 2

We can rewrite the above equation as

$U_2 - U_1 = q_p - p\,(V_2 - V_1)$

On rearranging, we get

$q_p = (U_2 + pV_2) - (U_1 + pV_1)$ (6.6)

Now we can define another thermodynamic function, the enthalpy H [Greek word enthalpien, to warm or heat content] as :

$H = U + pV$ (6.7)

so, equation (6.6) becomes

$q_p = H_2 - H_1 = \Delta H$

Although q is a path dependent function, H is a state function because it depends on U, p and V, all of which are state functions. Therefore, ΔH is independent of path. Hence, q_p is also independent of path.

For finite changes at constant pressure, we can write equation 6.7 as

$\Delta H = \Delta U + \Delta pV$

Since p is constant, we can write

$\Delta H = \Delta U + p\Delta V$ (6.8)

It is important to note that when heat is absorbed by the system at constant pressure, we are actually measuring changes in the enthalpy. Remember $\Delta H = q_p$, heat absorbed by the system at constant pressure.

ΔH **is negative for exothermic reactions which evolve heat during the reaction and** ΔH **is positive for endothermic reactions which absorb heat from the surroundings.**

At constant volume ($\Delta V = 0$), $\Delta U = q_V$, therefore equation 6.8 becomes

$\Delta H = \Delta U = q_V$

The difference between ΔH and ΔU is not usually significant for systems consisting of only solids and / or liquids. Solids and liquids do not suffer any significant volume changes upon heating. The difference, however, becomes significant when gases are involved. Let us consider a reaction involving gases. If V_A is the total volume of the gaseous reactants, V_B is the total volume of the gaseous products, n_A is the number of moles of gaseous reactants and n_B is the number of moles of gaseous products, all at constant pressure and temperature, then using the ideal gas law, we write,

$pV_A = n_ART$

and $pV_B = n_BRT$

Thus, $pV_B - pV_A = n_BRT - n_ART = (n_B - n_A)RT$

or $p\ (V_B - V_A) = (n_B - n_A)\ RT$

or $p\ \Delta V = \Delta n_g RT$ (6.9)

Here, Δn_g refers to the number of moles of gaseous products minus the number of moles of gaseous reactants.

Substituting the value of $p\Delta V$ from equation 6.9 in equation 6.8, we get

$\Delta H = \Delta U + \Delta n_g RT$ (6.10)

The equation 6.10 is useful for calculating ΔH from ΔU and vice versa.

Problem 6.5

If water vapour is assumed to be a perfect gas, molar enthalpy change for vapourisation of 1 mol of water at 1bar and 100°C is 41kJ mol–1. Calculate the internal energy change, when 1 mol of water is vapourised at 1 bar pressure and 100°C.

Solution

(i) The change $H_2O(l) \rightarrow H_2O(g)$

$\Delta H = \Delta U + \Delta n_g RT$

or $\Delta U = \Delta H - \Delta n_g RT$, substituting the values, we get

$\Delta U = 41.00\ \text{kJ mol}^{-1} - 1 \times 8.3\ \text{J mol}^{-1}\text{K}^{-1} \times 373\ \text{K}$

= 41.00 kJ mol-1 – 3.096 kJ mol-1

= 37.904 kJ mol–1

(b) Extensive and Intensive Properties

In thermodynamics, a distinction is made between extensive properties and intensive properties. An **extensive property** is a property whose value depends on the quantity or size of matter present in the system. For example, mass, volume, internal energy, enthalpy, heat capacity, etc.

are extensive properties.

Those properties which do not depend on the quantity or size of matter present are known as **intensive properties**. For example temperature, density, pressure etc. are intensive properties. A molar property, χ_m, is the value of an extensive property χ of the system for 1 mol of the substance. If n is the amount of matter, $C_m = \frac{C}{n}$ is independent of the amount of matter. Other examples are molar volume, V_m and molar heat capacity, C_m. Let us understand the distinction between extensive and intensive properties by considering a gas enclosed in a container of volume V and at temperature T [Fig. 6.6(a)]. Let us make a partition such that volume is halved, each part [Fig. 6.6 (b)] now has one half of the original volume, $\frac{V}{2}$, but the temperature will still remain the same i.e., T. It is clear that volume is an extensive property and temperature is an intensive property.

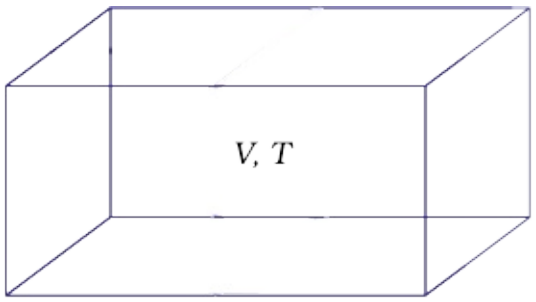


Fig. 6.6(a) A gas at volume V and temperature T

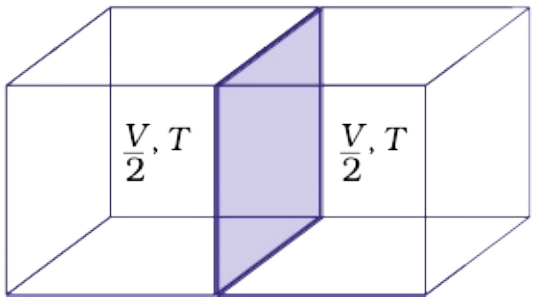


Fig. 6.6 (b) Partition, each part having half the volume of the gas

(c) Heat Capacity

In this sub-section, let us see how to measure heat transferred to a system. This heat appears as a rise in temperature of the system in case of heat absorbed by the system.

The increase of temperature is proportional to the heat transferred

$$q = coeff \times \Delta T$$

The magnitude of the coefficient depends on the size, composition and nature of the system. We can also write it as q = C ΔT

The coefficient, C is called the heat capacity.

Thus, we can measure the heat supplied by monitoring the temperature rise, provided we know the heat capacity.

When C is large, a given amount of heat results in only a small temperature rise. Water has a large heat capacity i.e., a lot of energy is needed to raise its temperature.

C is directly proportional to amount of substance. The molar heat capacity of a substance, $C_m = \left(\frac{C}{n}\right)$, is the heat capacity for one mole of the substance and is the quantity of heat needed to raise the temperature of one mole by one degree celsius (or one kelvin). Specific heat, also called specific heat capacity is the quantity of heat required to raise the temperature of one unit mass of a substance by one degree celsius (or one kelvin). For finding out the heat, q, required to raise the temperatures

of a sample, we multiply the specific heat of the substance, c, by the mass m, and temperatures change, ΔT as

$$q = c \times m \times \Delta T = C\,\Delta T \qquad (6.11)$$

(d) The Relationship between Cp and CV for an Ideal Gas

At constant volume, the heat capacity, C is denoted by C_V and at constant pressure, this is denoted by C_p . Let us find the relationship between the two.

We can write equation for heat, q

at constant volume as $q_v = C_v \Delta T = \Delta U$

at constant pressure as $q_p = C_p \Delta T = \Delta H$

The difference between C_p and C_v can be derived for an ideal gas as:

For a mole of an ideal gas, $\Delta H = \Delta U + \Delta(pV)$

$$= \Delta U + \Delta(RT)$$

$$= \Delta U + R\Delta T$$

$$\therefore\ \Delta H = \Delta U + R\,\Delta T \qquad (6.12)$$

On putting the values of ΔH and ΔU, we have

$$C_p \Delta T = C_v \Delta T + R\Delta T$$

$$C_p = C_V + R$$

$$C_p - C_v = R \qquad (6.13)$$

6.3 Measurement of ΔU and ΔH: Calorimetry

We can measure energy changes associated with chemical or physical processes by an experimental technique called calorimetry. In calorimetry, the process is carried out in a vessel called calorimeter, which is immersed in a known volume of a liquid. Knowing the heat capacity of the liquid in which calorimeter is immersed and the heat capacity of calorimeter, it is possible to determine the heat evolved in the process by measuring temperature changes. Measurements are made

under two different conditions:

i) at constant volume, qV

ii) at constant pressure, qp

(a) ∆U Measurements

For chemical reactions, heat absorbed at constant volume, is measured in a bomb calorimeter (Fig. 6.7). Here, a steel vessel (the bomb) is immersed in a water bath. The whole device is called calorimeter. The steel vessel is immersed in water bath to ensure that no heat is lost to the surroundings. A combustible substance is burnt in pure dioxygen supplied in the steel bomb. Heat evolved during the reaction is transferred to the water around the bomb and its temperature is monitored. Since the bomb calorimeter is sealed, its volume does not change i.e., the energy changes associated with reactions are measured at constant volume. Under these conditions, no work is done as the reaction is carried out at constant volume in the bomb calorimeter. Even for reactions involving gases, there is no work done as $\Delta V = 0$. Temperature change of the calorimeter produced by the completed reaction is then converted to q_V, by using the known heat capacity of the calorimeter with the help of equation 6.11.

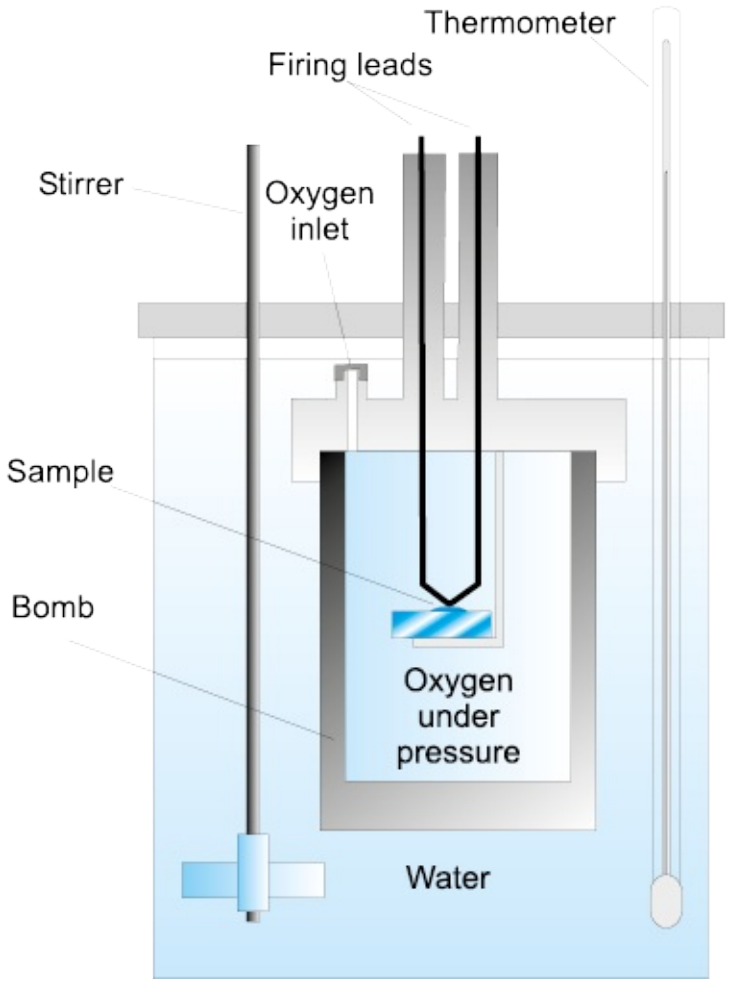


Fig. 6.7 Bomb calorimeter

(b) ΔH Measurements

Measurement of heat change at constant pressure (generally under atmospheric pressure) can be done in a calorimeter shown in Fig. 6.8. We know that $\Delta H = q_p$ (at constant p) and, therefore, heat absorbed or evolved, q_p at constant pressure is also called the heat of reaction or enthalpy of reaction, $\Delta_r H$.

In an exothermic reaction, heat is evolved, and system loses heat to the surroundings. Therefore, q_p will be negative and $\Delta_r H$ will also be negative. Similarly in an endothermic reaction, heat is absorbed, q_p is positive and $\Delta_r H$ will be positive.

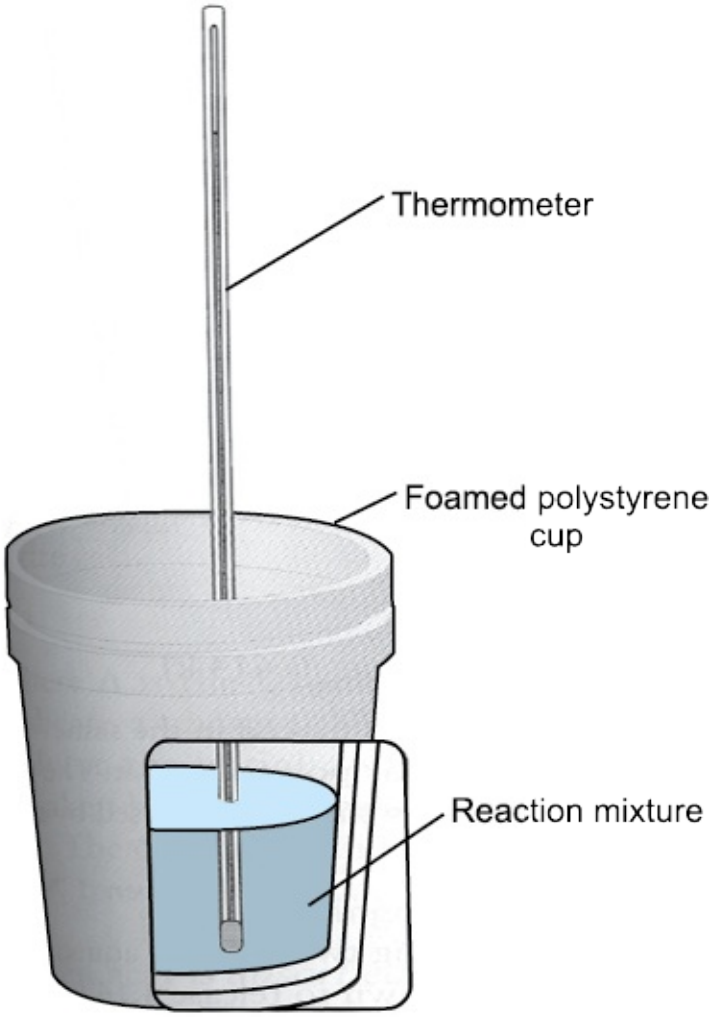


Fig. 6.8 Calorimeter for measuring heat changes at constant pressure (atmospheric pressure).

Problem 6.6

1g of graphite is burnt in a bomb calorimeter in excess of oxygen at 298 K and 1 atmospheric pressure according to the equation

C (graphite) + O_2 (g) → CO_2 (g)

During the reaction, temperature rises from 298 K to 299 K. If the heat capacity of the bomb calorimeter is 20.7kJ/K, what is the enthalpy change for the above reaction at 298 K and 1 atm?

Solution

Suppose q is the quantity of heat from the reaction mixture and C_V is the heat capacity of

the calorimeter, then the quantity of heat absorbed by the calorimeter.

$q = C_V \times \Delta T$

Quantity of heat from the reaction will have the same magnitude but opposite sign because the heat lost by the system (reaction mixture) is equal to the heat gained by the calorimeter.

$$q = -C_V \times \Delta T = -20.7\,\text{kJ/K} \times (299 - 298)\,\text{K}$$
$$= -20.7\,\text{kJ}$$

(Here, negative sign indicates the exothermic nature of the reaction)

Thus, ΔU for the combustion of the 1g of graphite = – 20.7 kJK–1

For combustion of 1 mol of graphite,

$$= \frac{12.0\ \text{g mol}^{-1} \times (-20.7\,\text{kJ})}{1\,\text{g}}$$

= – 2.48 ×102 kJ mol–1 , Since $\Delta n_g = 0$,

$\Delta H = \Delta U$ = – 2.48 ×102 kJ mol–1

6.4 Enthalpy change, ΔrH of a reaction – Reaction Enthalpy

In a chemical reaction, reactants are converted into products and is represented by,

Reactants → Products

The enthalpy change accompanying a reaction is called the **reaction enthalpy**. The enthalpy change of a chemical reaction, is given by the symbol $\Delta_r H$

$\Delta_r H$ = (sum of enthalpies of products) – (sum of enthalpies of reactants)

$$= \sum_i a_i H_{products} - \sum_i b_i H_{reactants} \quad (6.14)$$

Here symbol Σ (sigma) is used for summation and a_i and b_i are the stoichiometric coefficients of the products and reactants respectively in the balanced chemical equation. For example, for the reaction

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$$

$$\Delta_r H = \sum_i a_i H_{Products} - \sum_i b_i H_{reactants}$$

$= [H_m(CO_2, g) + 2H_m(H_2O, l)] - [H_m(CH_4, g) + 2H_m(O_2, g)]$

where H_m is the molar enthalpy.

Enthalpy change is a very useful quantity. Knowledge of this quantity is required when one needs to plan the heating or cooling required to maintain an industrial chemical reaction at constant temperature. It is also required to calculate temperature dependence of equilibrium constant.

(a) Standard Enthalpy of Reactions

Enthalpy of a reaction depends on the conditions under which a reaction is carried out. It is, therefore, necessary that we must specify some standard conditions. **The standard enthalpy of reaction is the enthalpy change for a reaction when all the participating substances are in their standard states.**

The standard state of a substance at a specified temperature is its pure form at 1 bar. For example, the standard state of liquid ethanol at 298 K is pure liquid ethanol at 1 bar; standard state of solid iron at 500 K is pure iron at 1 bar. Usually data are taken
at 298 K.

Standard conditions are denoted by adding the superscript 0 to the symbol ΔH, e.g., $\Delta H^{\ominus}$

(b) Enthalpy Changes during Phase Transformations

Phase transformations also involve energy changes. Ice, for example, requires heat for melting. Normally this melting takes place at constant pressure (atmospheric pressure) and during phase change, temperature remains constant (at 273 K).

$H_2O(s) \rightarrow H_2O(l)$; $\Delta_{fus}H^{\ominus} = 6.00$ kJ mol–1

Here $\Delta_{fus}H^{\ominus}$ is enthalpy of fusion in standard state. If water freezes, then process is reversed and equal amount of heat is given off to the surroundings.

The enthalpy change that accompanies melting of one mole of a solid substance in standard state is called standard enthalpy of fusion or molar enthalpy of fusion, $\Delta fusH^{\ominus}$**.**

Melting of a solid is endothermic, so all enthalpies of fusion are positive. Water requires heat for evaporation. At constant temperature of its boiling point T_b and at constant pressure:

Table 6.1 Standard Enthalpy Changes of Fusion and Vaporisation

Substance	T_f/K	$\Delta_{fus}H^{\ominus}$/(kJ mol^{-1})	T_b/K	$\Delta_{vap}H^{\ominus}$/(kJ mol^{-1})
N_2	63.15	0.72	77.35	5.59
NH_3	195.40	5.65	239.73	23.35
HCl	159.0	1.992	188.0	16.15
CO	68.0	6.836	82.0	6.04
CH_3COCH_3	177.8	5.72	329.4	29.1
CCl_4	250.16	2.5	349.69	30.0
H_2O	273.15	6.01	373.15	40.79
NaCl	1081.0	28.8	1665.0	170.0
C_6H_6	278.65	9.83	353.25	30.8

(T_f and T_b are melting and boiling points, respectively)

$H_2O(l) \rightarrow H_2O(g)$; $\Delta_{vap}H^{\ominus}$= + 40.79 kJ mol–1 $\Delta_{vap}H^{\ominus}$is the standard enthalpy of vaporisation.

Amount of heat required to vaporize one mole of a liquid at constant temperature and under standard pressure (1bar) is called its standard enthalpy of vaporization or molar enthalpy of vaporization,

$\Delta vap H^{\ominus}$.

Sublimation is direct conversion of a solid into its vapour. Solid CO_2 or 'dry ice' sublimes at 195K with $\Delta_{sub}H^{\ominus}$=25.2 kJ mol–1; naphthalene sublimes slowly and for this $\Delta_{sub} H^{\ominus}$ = 73.0 kJ mol–1 .

Standard enthalpy of sublimation, $\Delta_{sub}H^{\ominus}$ is the change in enthalpy when one mole of a solid substance sublimes at a constant temperature and under standard pressure (1bar).

The magnitude of the enthalpy change depends on the strength of the intermolecular interactions in the substance undergoing the phase transfomations. For example, the strong hydrogen bonds between water molecules hold them tightly in liquid phase. For an organic liquid, such as acetone, the intermolecular dipole-dipole interactions are significantly weaker. Thus, it requires less heat to vaporise 1 mol of acetone than it does to vaporize 1 mol of water. Table 6.1 gives values of standard enthalpy changes of fusion and vaporisation for some substances.

Problem 6.7

A swimmer coming out from a pool is covered with a film of water weighing about 18g. How much heat must be supplied to evaporate this water at

298 K ? Calculate the internal energy of vaporisation at 298K.

$\Delta_{vap} H^{\ominus}$ for water

at 298K= 44.01kJ mol–1

Solution

We can represent the process of evaporation as

$$\underset{1\,mol}{H_2O(l)} \xrightarrow{\text{vaporisation}} \underset{1\,mol}{H_2O(g)}$$

No. of moles in 18 g $H_2O(l)$ is

$$= \frac{18\,g}{18\,g\,mol^{-1}} = 1\,mol$$

Heat supplied to evaporate 18g water at 298 K $= n \times \Delta_{vap}H^{\ominus}$

$= (1\ mol) \times (44.01\ kJ\ mol^{-1})$

$= 44.01\ kJ$

(assuming steam behaving as an ideal gas).

$$\Delta_{vap}U = \Delta_{vap}H^{\ominus} - p\Delta V = \Delta_{vap}H^{\ominus} - \Delta n_g RT$$

$$\Delta_{vap}H^{v} - \Delta n_g\, RT = 44.01\ kJ$$

$$-(1)(8.314\ JK^{-1}mol^{-1})(298K)(10^{-3}kJ\,J^{-1})$$

$$\Delta_{vap}U^{v} = 44.01kJ - 2.48kJ$$

$$= 41.53\,kJ$$

Problem 6.8

Assuming the water vapour to be a perfect gas, calculate the internal energy change when 1 mol of water at 100°C and 1 bar pressure is converted to ice at 0°C. Given the enthalpy of fusion of ice is 6.00 kJ mol-1 heat capacity of water is 4.2 J/g°C

The change take place as follows:

Step - 1 1 mol H_2O (l, 100°C) ☾ 1 mol (l, 0°C) Enthalpy change ΔH_1

Step - 2 1 mol H_2O (l, 0°C) ☾ 1 mol H_2O(S, 0°C) Enthalpy change ΔH_2

Total enthalpy change will be -

$\Delta H = \Delta H_1 + \Delta H_2$

ΔH_1 = - (18 x 4.2 x 100) J mol-1

= - 7560 J mol-1 = - 7.56 k J mol-1

ΔH_2 = - 6.00 kJ mol-1

Therefore,

ΔH = - 7.56 kJ mol-1 + (-6.00 kJ mol-1) = -13.56 kJ mol-1

There is negligible change in the volume during the change form liquid to solid state.

Therefore, $p\Delta v = \Delta ng\ RT = 0$

$\Delta H = \Delta U = -\ 13.56 kJ\ mol\text{-}1$

Table 6.2 Standard Molar Enthalpies of Formation ($\Delta f\ H\ominus$) at 298K of a Few Selected Substances

Substance	$\Delta_f H^\ominus$ / (kJ mol^{-1})	Substance	$\Delta_f H^\ominus$ / (kJ mol^{-1})
$Al_2O_3(s)$	-1675.7	HI(g)	+26.48
$BaCO_3(s)$	-1216.3	KCl(s)	-436.75
$Br_2(l)$	0	KBr(s)	-393.8
$Br_2(g)$	+30.91	MgO(s)	-601.70
$CaCO_3(s)$	-1206.92	$Mg(OH)_2(s)$	-924.54
C (diamond)	+1.89	NaF(s)	-573.65
C (graphite)	0	NaCl(s)	-411.15
CaO(s)	- 635.09	NaBr(s)	-361.06
$CH_4(g)$	-74.81	NaI(s)	-287.78
$C_2H_4(g)$	52.26	$NH_3(g)$	-46.11
$CH_3OH(l)$	-238.86	NO(g)	+ 90.25
$C_2H_5OH(l)$	-277.69	$NO_2(g)$	+33.18
$C_6H_6(l)$	+ 49.0	$PCl_3(l)$	-319.70
CO(g)	-110.53	$PCl_5(s)$	-443.5
$CO_2(g)$	-393.51	$SiO_2(s)$ (quartz)	-910.94
$C_2H_6(g)$	-84.68	$SnCl_2(s)$	-325.1
$Cl_2(g)$	0	$SnCl_4(l)$	-511.3
$C_3H_8(g)$	-103.85	$SO_2(g)$	-296.83
$n-C_4H_{10}(g)$	-126.15	$SO_3(g)$	-395.72
HgS(s) red	-58.2	$SiH_4(g)$	+ 34
$H_2(g)$	0	$SiCl_4(g)$	-657.0
$H_2O(g)$	-241.82	C(g)	+716.68
$H_2O(l)$	-285.83	H(g)	+217.97
HF(g)	-271.1	Cl(g)	+121.68
HCl(g)	-92.31	$Fe_2O_3(s)$	–824.2
HBr(g)	-36.40		

(c) Standard Enthalpy of Formation

The standard enthalpy change for the formation of one mole of a compound from its elements in their most stable states of aggregation (also known as reference states) is called Standard Molar Enthalpy of Formation. Its symbol is ΔfH0, where the subscript ‘

f ’ indicates that one mole of the compound in question has been formed in its standard state from its elements in their most stable states of aggregation. The reference state of an element is its most stable state of aggregation at 25°C and 1 bar pressure.

For example, the reference state of dihydrogen is H_2 gas and those of dioxygen, carbon and sulphur are O_2 gas, $C_{graphite}$ and $S_{rhombic}$ respectively. Some reactions with standard molar enthalpies of formation are as follows.

$H_2(g) + ½O_2(g) \rightarrow H_2O(1)$;

$\Delta_f H^{\ominus} = –285.8$ kJ mol–1

C (graphite, s) + $2H_2(g) \rightarrow Ch_4$ (g);

$\Delta_f H^{\ominus} = –74.81$ kJ mol–1

2C (graphite, s)+$3H_2$ (g)+ $½O_2(g) \rightarrow C_2H_5OH(1)$;

$\Delta_f H^{\ominus} = – 277.7$kJ mol–1

It is important to understand that a standard molar enthalpy of formation, $\Delta_f H^{\ominus}$, is just a special case of $\Delta_r H^{\ominus}$, where one mole of a compound is formed from its constituent elements, as in the above three equations, where 1 mol of each, water, methane and ethanol is formed. In contrast, the enthalpy change for an exothermic reaction:

$CaO(s) + CO_2(g) \rightarrow CaCo_3(s)$;

$\Delta_r H^{\ominus} = – 178.3$kJ mol–1

is not an enthalpy of formation of calcium carbonate, since calcium carbonate has been formed from other compounds, and not from its constituent elements. Also, for the reaction given below, enthalpy change is not standard enthalpy of formation, $\Delta_f H^{\ominus}$ for HBr(g).

$H_2(g) + Br_2(l) \rightarrow 2HBr(g)$;

$\Delta_r H^{\ominus} = -178.3 kJ\ mol^{-1}$

Here two moles, instead of one mole of the product is formed from the elements, i.e., .

$\Delta_r H^{\ominus} = 2\Delta_f H^{\ominus}$

Therefore, by dividing all coefficients in the balanced equation by 2, expression for enthalpy of formation of HBr (g) is written as

$\frac{1}{2}H_2(g) + \frac{1}{2}Br_2(1) \rightarrow HBr(g)$;

$\Delta_f H^{\ominus} = -36.4\ kJ\ mol^{-1}$

Standard enthalpies of formation of some common substances are given in Table 6.2.

By convention, standard enthalpy for formation, $\Delta_f H^{\ominus}$, of an element in reference state, i.e., its most stable state of aggregation is taken as zero.

Suppose, you are a chemical engineer and want to know how much heat is required to decompose calcium carbonate to lime and carbon dioxide, with all the substances in their standard state.

$CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$; $\Delta_r H^{\ominus} = ?$

Here, we can make use of standard enthalpy of formation and calculate the enthalpy change for the reaction. The following general equation can be used for the enthalpy change calculation.

$$\Delta_r H^{\ominus} = \sum_i a_i \Delta_f H^{\ominus}(\text{products}) - \sum_i b_i \Delta_f H^{\ominus}(\text{reactants}) \quad (6.15)$$

where a and b represent the coefficients of the products and reactants in the balanced equation. Let us apply the above equation for decomposition of calcium carbonate. Here, coefficients ‘a’ and ‘b’ are 1 each. Therefore,

$\Delta_r H^{\ominus} = \Delta_f H^{\ominus} = [CaO(s)] + \Delta_f H^{\ominus}[CO_2(g)]$

$-\Delta_f H^{\ominus} = [CaCO_3(s)]$

$=1\ (-635.1\ kJ\ mol-1) + 1(-393.5\ kJ\ mol-1)$

$-1(-1206.9\ kJ\ mol-1)$

$= 178.3\ kJ\ mol-1$

Thus, the decomposition of $CaCO_3$ (s) is an endothermic process and you have to heat it for getting the desired products.

(d) Thermochemical Equations

A balanced chemical equation together with the value of its $\Delta_r H$ is called a thermochemical equation. We specify the physical state (alongwith allotropic state) of the substance in an equation. For example:

$C_2H_5OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l);$

$\Delta_r H^{\ominus} = -1367\ kJ\ mol-1$

The above equation describes the combustion of liquid ethanol at constant temperature and pressure. The negative sign of enthalpy change indicates that this is an exothermic reaction.

It would be necessary to remember the following conventions regarding thermo-chemical equations.

1. The coefficients in a balanced thermo-chemical equation refer to the number of moles (never molecules) of reactants and products involved in the reaction.

2. The numerical value of $\Delta_r H^{\ominus}$ refers to the number of moles of substances specified by an equation. Standard enthalpy change $\Delta_r H^{\ominus}$ will have units as kJ mol–1.

To illustrate the concept, let us consider the calculation of heat of reaction for the following reaction :

$$Fe_2O_3(s) + 3H_2(g) \rightarrow 2Fe(s) + 3H_2O(l),$$

From the Table (6.2) of standard enthalpy of formation ($\Delta_f H^{\ominus}$), we find :

$\Delta_f H^{\ominus}$ (H_2O,l) = –285.83 kJ mol–1;

$\Delta_f H^{\ominus}$ (Fe_2O_3,s) = – 824.2 kJ mol–1;

Also $\Delta_f H^{\ominus}$ (Fe, s) = 0 and

$\Delta_f H^{\ominus}$ (H_2, g) = 0 as per convention

Then,

$\Delta_f H_1^{\ominus}$ = 3(–285.83 kJ mol–1)

– 1(– 824.2 kJ mol–1)

= (–857.5 + 824.2) kJ mol–1

= –33.3 kJ mol–1

Note that the coefficients used in these calculations are pure numbers, which are equal to the respective stoichiometric coefficients. The unit for $\Delta_r H^{\ominus}$ is

kJ mol–1, which means per mole of reaction. Once we balance the chemical equation in a particular way, as above, this defines the mole of reaction. If we had balanced the equation differently, for example,

$$\frac{1}{2}Fe_2O_3(s) + \frac{3}{2}H_2(g) \rightarrow Fe(s) + \frac{3}{2}H_2O(l)$$

then this amount of reaction would be one mole of reaction and $\Delta_r H^{\ominus}$ would be

$\Delta_f H_2^{\ominus} = \frac{3}{2}$ (–285.83 kJ mol–1)

$-\frac{1}{2}$ (–824.2 kJ mol–1)

= (– 428.7 + 412.1) kJ mol–1

= –16.6 kJ mol–1 = ½ $\Delta_r H_1^{\ominus}$

It shows that enthalpy is an extensive quantity.

3. When a chemical equation is reversed, the value of $\Delta_r H^{\ominus}$ is reversed in sign. For example

$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$;

$\Delta_r H^{\ominus} = -91.8$ kJ. mol–1

$2NH_3(g) \rightarrow N_2(g) + 3H_2(g)$;

$\Delta_r H^{\ominus} = +91.8$ kJ mol–1

(e) Hess's Law of Constant Heat Summation

We know that enthalpy is a state function, therefore the change in enthalpy is independent of the path between initial state (reactants) and final state (products). In other words, enthalpy change for a reaction is the same whether it occurs in one step or in a series of steps. This may be stated as follows in the form of Hess's Law.

If a reaction takes place in several steps then its standard reaction enthalpy is the sum of the standard enthalpies of the intermediate reactions into which the overall reaction may be divided at the same temperature.

Let us understand the importance of this law with the help of an example. Consider the enthalpy change for the reaction

$$C\ (graphite,s) + \frac{1}{2} O_2\ (g) \rightarrow CO\ (g);\ \Delta_r H^{\ominus} = ?$$

Although CO(g) is the major product, some CO_2 gas is always produced in this reaction. Therefore, we cannot measure enthalpy change for the above reaction directly. However, if we can find some other reactions involving related species, it is possible to calculate the enthalpy change for the above reaction.

Let us consider the following reactions:

$C\ (graphite,s) + O_2\ (g) \rightarrow CO_2\ (g)$;

$\Delta_r H^{\ominus}$= – 393.5 kJ mol–1 (i)

$$CO\ (g) + \frac{1}{2} O_2\ (g) \rightarrow CO_2\ (g)$$

$\Delta_r H^{\ominus}$= – 283.0 kJ mol–1 (ii)

We can combine the above two reactions in such a way so as to obtain the desired reaction. To get one mole of CO(g) on the right, we reverse equation (ii). In this, heat is absorbed instead of being released, so we change sign of $\Delta_r H^{\ominus}$ value

$$CO_2\ (g) \rightarrow CO\ (g) + \frac{1}{2} O_2\ (g);$$

$\Delta_r H^{\ominus}$= + 283.0 kJ mol–1 (iii)

Adding equation (i) and (iii), we get the desired equation,

$$C(\text{graphite, s}) + \frac{1}{2} O_2\,(g) \rightarrow CO\,(g);$$

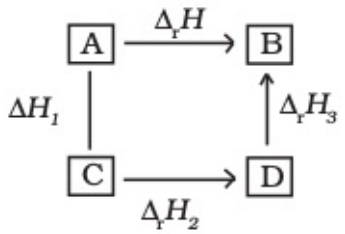
for which $\Delta_r H^{\ominus}$ = (– 393.5 + 283.0)

= – 110.5 kJ mol–1

In general, if enthalpy of an overall reaction A→B along one route is $\Delta_r H$ and $\Delta_r H_1$, $\Delta_r H_2$, $\Delta_r H_3$..... representing enthalpies of reactions leading to same product, B along another route,then we have

$\Delta_r H = \Delta_r H_1 + \Delta_r H_2 + \Delta_r H_3$ ... (6.16)

It can be represented as:



6.5 Enthalpies for different types of reactions

It is convenient to give name to enthalpies specifying the types of

reactions.

(a) Standard Enthalpy of Combustion (symbol : $\Delta_c H^{\ominus}$)

Combustion reactions are exothermic in nature. These are important in industry, rocketry, and other walks of life. Standard enthalpy of combustion is defined as the enthalpy change per mole (or per unit amount) of a substance, when it undergoes combustion and all the **reactants and products** being in their standard states at the specified temperature.

Cooking gas in cylinders contains mostly butane (C_4H_{10}). During complete combustion of one mole of butane, 2658 kJ of heat is released. We can write the thermochemical reactions for this as:

$$C_4H_{10}(g) + \frac{13}{2}O_2(g) \rightarrow 4CO_2(g) + 5H_2O(l);$$
$$\Delta_c H^{\ominus} = -2658.0 \text{ kJ mol}^{-1}$$

Similarly, combustion of glucose gives out 2802.0 kJ/mol of heat, for which the overall equation is :

$$C_6H_{12}O_6(g) + 6O_2(g) \rightarrow 6CO_2(g) + 6H_2O(l);$$
$$\Delta_c H^{\ominus} = -2802.0 \text{ kJ mol}^{-1}$$

Our body also generates energy from food by the same overall process as combustion, although the final products are produced after a series of complex bio-chemical reactions involving enzymes.

Problem 6.9

The combustion of one mole of benzene takes place at 298 K and 1 atm. After combustion, CO_2(g) and H_2O (1) are produced and 3267.0 kJ of heat is liberated. Calculate the standard enthalpy of formation, $\Delta_f H^{\ominus}$ of benzene. Standard enthalpies of formation of CO_2(g) and $H_2O(l)$ are –393.5 kJ mol–1 and – 285.83 kJ mol–1 respectively.

Solution

The formation reaction of benezene is given by :

$$6C(\text{graphite}) + 3H_2(g) \rightarrow C_6H_6(l);$$

$$\Delta_f H^{\ominus} = ? \ldots \text{(i)}$$

The enthalpy of combustion of 1 mol of benzene is :

$$C_6H_6(l) + \frac{15}{2}O_2 \rightarrow 6CO_2(g) + 3H_2O(l);$$

$$\Delta_c H^{\ominus} = -3267 \text{ kJ mol}^{-1} \ldots \text{(ii)}$$

The enthalpy of formation of 1 mol of $CO_2(g)$:

$$C(\text{graphite}) + O_2(g) \rightarrow CO_2(g);$$

$$\Delta_f H^{\ominus} = -393.5 \text{ kJ mol}^{-1} \ldots \text{(iii)}$$

The enthalpy of formation of 1 mol of $H_2O(l)$ is :

$$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l);$$

$$\Delta_c H^{\ominus} = -285.83 \text{ kJ mol}^{-1} \ldots \text{(iv)}$$

multiplying eqn. (iii) by 6 and eqn. (iv) by 3 we get:

$$6C(\text{graphite}) + 6O_2(g) \rightarrow 6CO_2(g);$$
$$\Delta_f H^{\ominus} = -2361 \text{ kJ mol}^{-1}$$

$$3H_2(g) + \frac{3}{2}O_2(g) \rightarrow 3H_2O(l);$$
$$\Delta_f H^{\ominus} = -857.49 \text{ kJ mol}^{-1}$$

Summing up the above two equations :

$$6C(\text{graphite}) + 3H_2(g) + \frac{15}{2}O_2(g) \rightarrow 6CO_2(g) + 3H_2O(l);$$
$$\Delta_f H^{\ominus} = -3218.49 \text{ kJ mol}^{-1} \ldots \text{(v)}$$

Reversing equation (ii);

$$6CO_2(g) + 3H_2O(l) \rightarrow C_6H_6(l) + \frac{15}{2}O_2;$$
$$\Delta_f H^{\ominus} = -3267.0 \text{ kJ mol}^{-1} \ldots \text{(vi)}$$

Adding equations (v) and (vi), we get

$$6C(\text{graphite}) + 3H_2(g) \rightarrow C_6H_6(l);$$
$$\Delta_f H^{\ominus} = -48.51 \text{ kJ mol}^{-1} \ldots \text{(iv)}$$

(b) Enthalpy of Atomization (symbol: $\Delta_a H^{\ominus}$)

Consider the following example of atomization of dihydrogen

$H_2(g) \rightarrow 2H(g)$; $\Delta_a H^{\ominus}$ = 435.0 kJ mol–1

You can see that H atoms are formed by breaking H–H bonds in dihydrogen. The enthalpy change in this process is known as enthalpy of atomization, $\Delta_a H^{\ominus}$. It is the enthalpy change on breaking one mole of bonds completely to obtain atoms in the gas phase.

In case of diatomic molecules, like dihydrogen (given above), the enthalpy of atomization is also the bond dissociation enthalpy. The other examples of enthalpy of atomization can be

$CH_4(g) \rightarrow C(g) + 4H(g)$; $\Delta_a H^{\ominus}$ = 1665 kJ mol–1

Note that the products are only **atoms** of C and H in gaseous phase. Now see the following reaction:

$Na(s) \rightarrow Na(g)$; $\Delta_a H^{\ominus}$ = 108.4 kJ mol–1

In this case, the enthalpy of atomization is same as the enthalpy of sublimation.

(c) Bond Enthalpy (symbol: $\Delta_{bond} H^{\ominus}$)

Chemical reactions involve the breaking and making of chemical bonds. Energy is required to break a bond and energy is released when a bond is formed. It is possible to relate heat of reaction to changes in energy associated with breaking and making of chemical bonds. With reference to the enthalpy changes associated with chemical bonds, two different terms are used in thermodynamics.

(i) Bond dissociation enthalpy

(ii) Mean bond enthalpy

Let us discuss these terms with reference to diatomic and polyatomic molecules.

Diatomic Molecules: Consider the following process in which the bonds in one mole of dihydrogen gas (H_2) are broken:

$H_2(g) \rightarrow 2H(g)$; $\Delta_{H-H} H^{\ominus}$ = 435.0 kJ mol–1

The enthalpy change involved in this process is the bond dissociation enthalpy of H–H bond. The bond dissociation enthalpy is the change in enthalpy when one mole of covalent bonds of a gaseous covalent compound is broken to form products in the gas phase.

Note that it is the same as the enthalpy of atomization of dihydrogen. This is true for all diatomic molecules. For example:

$Cl_2(g) \rightarrow 2Cl(g)$; $\Delta_{Cl-Cl} H^{\ominus}$ = 242 kJ mol–1

$O_2(g) \rightarrow 2O(g)$; $\Delta_{O=O}H^{\ominus}$ = 428 kJ mol–1

In the case of polyatomic molecules, bond dissociation enthalpy is different for different bonds within the same molecule.

Polyatomic Molecules: Let us now consider a polyatomic molecule like methane, CH_4. The overall thermochemical equation for its atomization reaction is given below:

$$CH_4(g) \rightarrow C(g) + 4H(g);$$

$\Delta_a H^{\ominus}$ = 1665 kJ mol–1

In methane, all the four C – H bonds are identical in bond length and energy. However, the energies required to break the individual C – H bonds in each successive step differ :

$CH_4(g) \rightarrow CH_3(g)+H(g); \Delta_{bond} H^{\ominus}$= +427 kJ mol–1

$CH_3(g) \rightarrow CH_2(g)+H(g); \Delta_{bond} H^{\ominus}$= +439 kJ mol–1

$CH_2(g) \rightarrow CH(g)+H(g); \Delta_{bond} H^{\ominus}$= +452 kJ mol–1

$CH(g) \rightarrow C(g)+H(g); \Delta_{bond} H^{\ominus}$= +347 kJ mol–1

Therefore,

$CH_4(g) \rightarrow C(g)+4H(g); \Delta_a H^{\ominus}$= 1665 kJ mol–1

In such cases we use **mean bond enthalpy of C – H bond**.

For example in CH_4, $\Delta_{C-H}H^{\ominus}$ is calculated as:

$\Delta_{C-H}H^{\ominus}$= ¼ ($\Delta_a H^{\ominus}$) = ¼ (1665 kJ mol–1)

= 416 kJ mol–1

We find that mean C–H bond enthalpy in methane is 416 kJ/mol. It has been found that mean C–H bond enthalpies differ slightly from compound to compound, as in CH_3CH_2Cl,CH_3NO_2, etc, but it does not differ in a great deal*. Using Hess's law, bond enthalpies can be calculated. Bond

enthalpy values of some single and multiple bonds are given in Table 6.3. The reaction enthalpies are very important quantities as these arise from the changes that accompany the breaking of old bonds and formation of the new bonds. We can predict enthalpy of a reaction in gas phase, if we know different bond enthalpies. The standard enthalpy of reaction, $\Delta_r H^{\ominus}$ is related to bond enthalpies of the reactants and products in gas phase reactions as:

$$\Delta_r H^{\ominus} = \sum \text{bond enthalpies}_{reactants} - \sum \text{bond enthalpies}_{products} \quad (6.17)^{**}$$

This relationship is particularly more useful when the required values of $\Delta_f H^{\ominus}$ are not available. The net enthalpy change of a reaction is the amount of energy required to break all the bonds in the reactant molecules minus the amount of energy required to break all the bonds in the product molecules. Remember that this relationship is approximate and is valid when all substances (reactants and products) in the reaction are in gaseous state.

Table 6.3(a) Some Mean Single Bond Enthalpies in kJ mol^{-1} at 298 K

H	C	N	O	F	Si	P	S	Cl	Br	I	
435.8	414	389	464	569	293	318	339	431	368	297	H
	347	293	351	439	289	264	259	330	276	238	C
		159	201	272	-	209	-	201	243	-	N
			138	184	368	351	-	205	-	201	O
				155	540	490	327	255	197	-	F
					176	213	226	360	289	213	Si
						213	230	331	272	213	P
							213	251	213	-	S
								243	218	209	Cl
									192	180	Br
										151	I

Table 6.3(b) Some Mean Multiple Bond Enthalpies in kJ mol^{-1} at 298 K

N = N	418	C = C	611	O = O	498
N ≡ N	946	C ≡ C	837		
C = N	615	C = O	741		
C ≡ N	891	C ≡ O	1070		

* *Note that symbol used for bond dissociation enthalpy and mean bond enthalpy is the same.*

** *If we use enthalpy of bond formation, ($\Delta_f H_{bond}^{\ominus}$), which is the enthalpy change when one mole of a particular type of bond is formed from gaseous atom, then* $\Delta_f H^{\ominus} = \sum \Delta_f H^{\ominus}_{\text{bonds of products}} - \sum \Delta_f H^{\ominus}_{\text{bonds of reactants}}$

(d) Lattice Enthalpy

The lattice enthalpy of an ionic compound is the enthalpy change which occurs when one mole of an ionic compound dissociates into its ions in gaseous state.

$$Na^+Cl^-(s) \rightarrow Na^+(g) + Cl^-(g);$$

$$\Delta_{lattice}H^{\ominus} = +788 \text{ kJ mol}^{-1}$$

Since it is impossible to determine lattice enthalpies directly by experiment, we use an indirect method where we construct an enthalpy diagram called a **Born-Haber Cycle** (Fig. 6.9).

Let us now calculate the lattice enthalpy of Na+Cl–(s) by following steps given below :

1. Na (s) → Na (g), sublimation of sodium metal, $\Delta_{sub}H^{\ominus}$= 108.4 kJ

mol–1

2. Na (g) → Na^+ (g) + e^{-1}(g) ,, the ionization of sodium atoms, ionization enthalpy $\Delta_i H^{\ominus}$= 496 kJ mol–1

3. $\frac{1}{2}Cl_2(g) \rightarrow Cl(g)$, the dissociation of chlorine, the reaction enthalpy is half the bond dissociation enthalpy.

$\frac{1}{2}\Delta_{bond}H^{\ominus} = 121 \text{ kJ mol}^{-1}$

4. $Cl(g) + e^{-1}(g) \rightarrow C\bar{l}(g)$ electron gained by chlorine atoms. The electron gain enthalpy, Δ_{eg}H 0 = – 348.6 kJ mol–1.

You have learnt about ionization enthalpy and electron gain enthalpy in Unit 3. In fact, these terms have been taken from thermodynamics. Earlier terms, ionization energy and electron affinity were in practice in place of the above terms (see the box for justification).

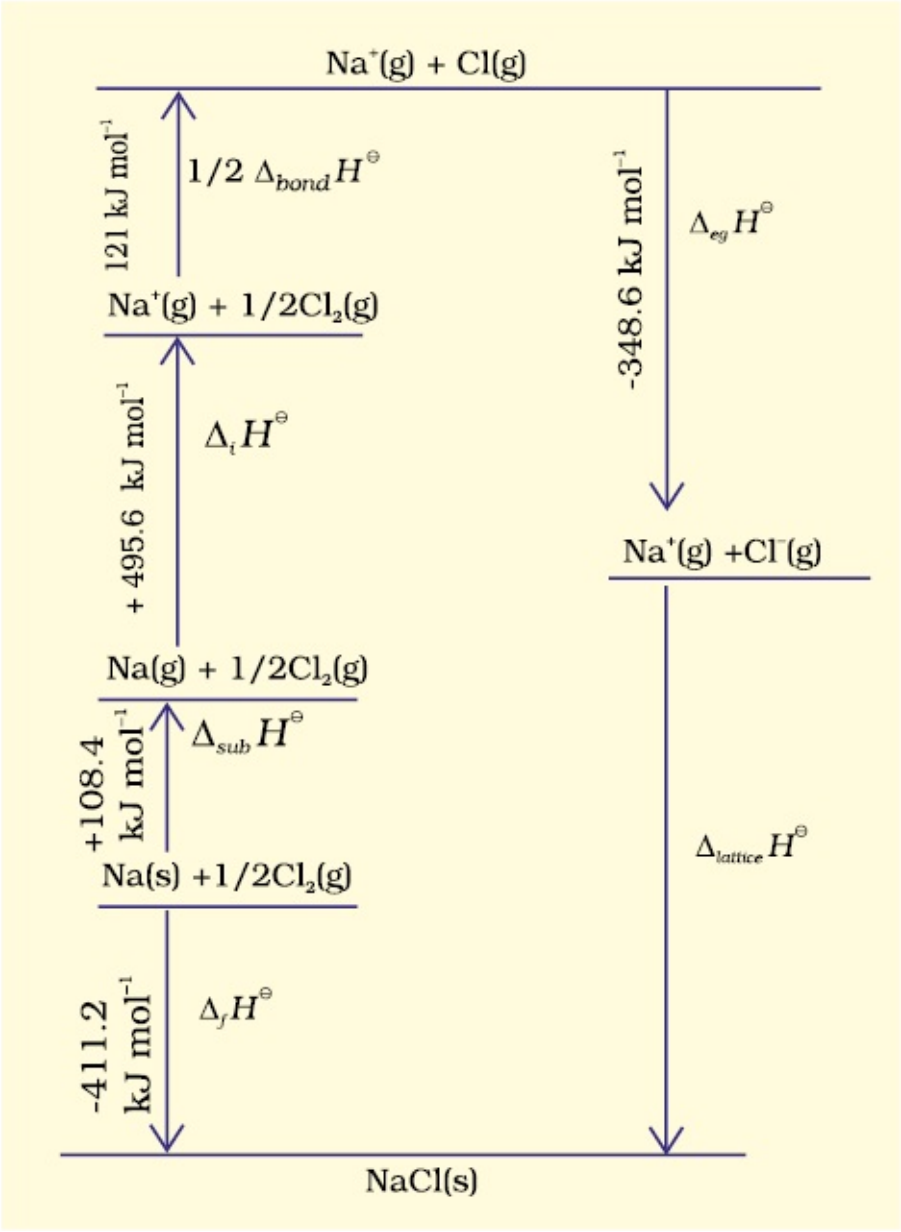


Fig. 6.9 Enthalpy diagram for lattice enthalpy of NaCl

Ionization Energy and Electron Affinity

Ionization energy and electron affinity are defined at absolute zero. At any other temperature, heat capacities for the reactants and the products have to be taken into account. Enthalpies of reactions for

M(g) → M+(g) + e– (for ionization)

M(g) + e– → M–(g) (for electron gain)

at temperature, T is

$$\Delta_r H^{\ominus}(T) = \Delta_r H^{\ominus}(0) + \int_0^T \Delta_r C_P^{\ominus} dT$$

The value of C_p for each species in the above reaction is 5/2 R (C_V = 3/2R)

So, $\Delta_r C_p^{\ominus}$ = + 5/2 R (for ionization)

$\Delta_r C_p^{\ominus}$ = – 5/2 R (for electron gain)

Therefore,

$\Delta_r H0$ (ionization enthalpy)

= E_0 (ionization energy) + 5/2 RT

$\Delta_r H0$ (electron gain enthalpy)

= – A(electron affinity) – 5/2 RT

5. $Na^+(g) + Cl^-(g) \rightarrow Na^+Cl^-(s)$

The sequence of steps is shown in Fig. 6.9, and is known as a Born-Haber cycle. The importance of the cycle is that, the sum of the enthalpy changes round a cycle is zero. Applying Hess's law, we get,

$\Delta_{lattice}H^{\ominus}$= 411.2 + 108.4 + 121 + 496 – 348.6

$\Delta_{lattice}H^{\ominus}$= + 788kJ

for NaCl(s) d Na+(g) + Cl–(g)

Internal energy is smaller by 2RT (because Δn_g = 2) and is equal to + 783 kJ mol–1.

Now we use the value of lattice enthalpy to calculate enthalpy of solution from the expression:

$\Delta_{sol}H^{\ominus}$= $\Delta_{lattice}H^{\ominus}$+ $\Delta_{hyd}H^{\ominus}$

For one mole of NaCl(s),

lattice enthalpy = + 788 kJ mol–1

and $\Delta_{hyd}H^{\ominus}$ = – 784 kJ mol–1(from the literature)

$\Delta_{sol}H^{\ominus}$ = + 788 kJ mol–1 – 784 kJ mol–1

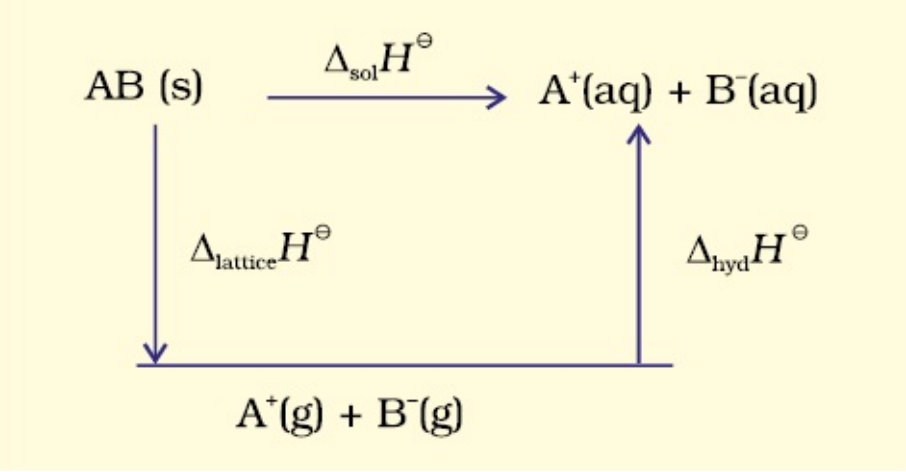
= + 4 kJ mol–1

The dissolution of NaCl(s) is accompanied by very little heat change.

(e) Enthalpy of Solution (symbol : $\Delta_{sol}H^{\ominus}$)

Enthalpy of solution of a substance is the enthalpy change when one mole of it dissolves in a specified amount of solvent. The enthalpy of solution at infinite dilution is the enthalpy change observed on dissolving the substance in an infinite amount of solvent when the interactions between the ions (or solute molecules) are negligible.

When an ionic compound dissolves in a solvent, the ions leave their ordered positions on the crystal lattice. These are now more free in solution. But solvation of these ions (hydration in case solvent is water) also occurs at the same time. This is shown diagrammatically, for an ionic compound, AB (s)



The enthalpy of solution of AB(s), $\Delta_{sol}H^{\ominus}$, in water is, therefore, determined by the selective values of the lattice enthalpy,$\Delta_{lattice}H^{\ominus}$ and enthalpy of hydration of ions, $\Delta_{hyd}H^{\ominus}$ as

$\Delta_{sol}H^{\ominus} = \Delta_{lattice}H^{\ominus} + \Delta_{hyd}H^{\ominus}$

For most of the ionic compounds, $\Delta_{sol} H^{\ominus}$ is positive and the dissociation process is endothermic. Therefore the solubility of most salts in water increases with rise of temperature. If the lattice enthalpy is very high, the dissolution of the compound may not take place at all. Why do many fluorides tend to be less soluble than the corresponding chlorides? Estimates of the magnitudes of enthalpy changes may be made by using tables of bond energies (enthalpies) and lattice energies (enthalpies).

(f) Enthalpy of Dilution

It is known that enthalpy of solution is the enthalpy change associated with the addition of a specified amount of solute to the specified amount of solvent at a constant temperature and pressure. This argument can be applied to any solvent with slight modification. Enthalpy change for dissolving one mole of gaseous hydrogen chloride in 10 mol of water can be represented by the following equation. For convenience we will use the symbol aq. for water

$HCl(g) + 10\ aq. \rightarrow HCl.10\ aq.$

$\Delta H = -69.01$ kJ / mol

Let us consider the following set of enthalpy changes:

(S-1) $HCl(g) + 25\ aq. \rightarrow HCl.25\ aq.$ $\Delta H = -72.03$ kJ / mol

(S-2) $HCl(g) + 40\ aq. \rightarrow HCl.40\ aq.$ $\Delta H = -72.79$ kJ / mol

(S-3) $HCl(g) + \infty\ aq. \rightarrow HCl.\ \infty\ aq.$ $\Delta H = -74.85$ kJ / mol

The values of ΔH show general dependence of the enthalpy of solution on amount of solvent. As more and more solvent is used, the enthalpy of solution approaches a limiting value, i.e, the value in infinitely dilute solution. For hydrochloric acid this value of ΔH is given above in equation (S-3).

If we subtract the first equation (equation S-1) from the second equation (equation S-2) in the above set of equations, we obtain–

$HCl.25\ aq. + 15\ aq. \rightarrow HCl.40\ aq.$

ΔH = [–72.79 – (–72.03)] kJ / mol

= – 0.76 kJ / mol

This value (–0.76kJ/mol) of ΔH is enthalpy of dilution. It is the heat withdrawn from the surroundings when additional solvent is added to the solution. The enthalpy of dilution of a solution is dependent on the original concentration of the solution and the amount of solvent added.

6.6 spontaneity

The first law of thermodynamics tells us about the relationship between the heat absorbed and the work performed on or by a system. It puts no restrictions on the direction of heat flow. However, the flow of heat is unidirectional from higher temperature to lower temperature. In fact, all naturally occurring processes whether chemical or physical will tend to proceed spontaneously in one direction only. For example, a gas expanding to fill the available volume, burning carbon in dioxygen giving carbon dioxide.

But heat will not flow from colder body to warmer body on its own, the gas in a container will not spontaneously contract into one corner or carbon dioxide will not form carbon and dioxygen spontaneously. These and many other spontaneously occurring changes show unidirectional change. We may ask ‘what is the driving force of spontaneously occurring changes ? What determines the direction of a spontaneous change ? In this section, we shall establish some criterion for these processes whether these will take place or not.

Let us first understand what do we mean by spontaneous reaction or change ? You may think by your common observation that spontaneous reaction is one which occurs immediately when contact is made between the reactants. Take the case of combination of hydrogen and oxygen. These gases may be mixed at room temperature and left for many years without observing any perceptible change. Although the reaction is taking

place between them, it is at an extremely slow rate. It is still called spontaneous reaction. So spontaneity means 'having the potential to proceed without the assistance of external agency'. However, it does not tell about the rate of the reaction or process. Another aspect of spontaneous reaction or process, as we see is that these cannot reverse their direction on their own. We may summarise it as follows:

A spontaneous process is an irreversible process and may only be reversed by some external agency.

(a) Is Decrease in Enthalpy a Criterion for Spontaneity ?

If we examine the phenomenon like flow of water down hill or fall of a stone on to the ground, we find that there is a net decrease in potential energy in the direction of change. By analogy, we may be tempted to state that a chemical reaction is spontaneous in a given direction, because decrease in energy has taken place, as in the case of exothermic reactions. For example:

$$\frac{1}{2}N_2(g) + \frac{3}{2}H_2(g) = NH_3(g) ;$$

$\Delta_r H^{\ominus}$ = – 46.1 kJ mol–1

$$\frac{1}{2}H_2(g) + \frac{1}{2}Cl_2(g) = HCl\ (g) ;$$

$\Delta_r H^{\ominus}$ = – 92.32 kJ mol–1

$$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l) ;$$

$\Delta_r H^{\ominus}$ = –285.8 kJ mol–1

The decrease in enthalpy in passing from reactants to products may be shown for any exothermic reaction on an enthalpy diagram as shown in Fig. 6.10(a).

Thus, the postulate that driving force for a chemical reaction may be due

to decrease in energy sounds ‘reasonable’ as the basis of evidence so far !

Now let us examine the following reactions:

$\frac{1}{2}$ $N_2(g) + O_2(g) \rightarrow NO_2(g)$;

$\Delta_r H^{\ominus} = +33.2$ kJ mol–1

$C(graphite, s) + 2\ S(l) \rightarrow CS_2(l)$;

$\Delta_r H^{\ominus} = +128.5$ kJ mol–1

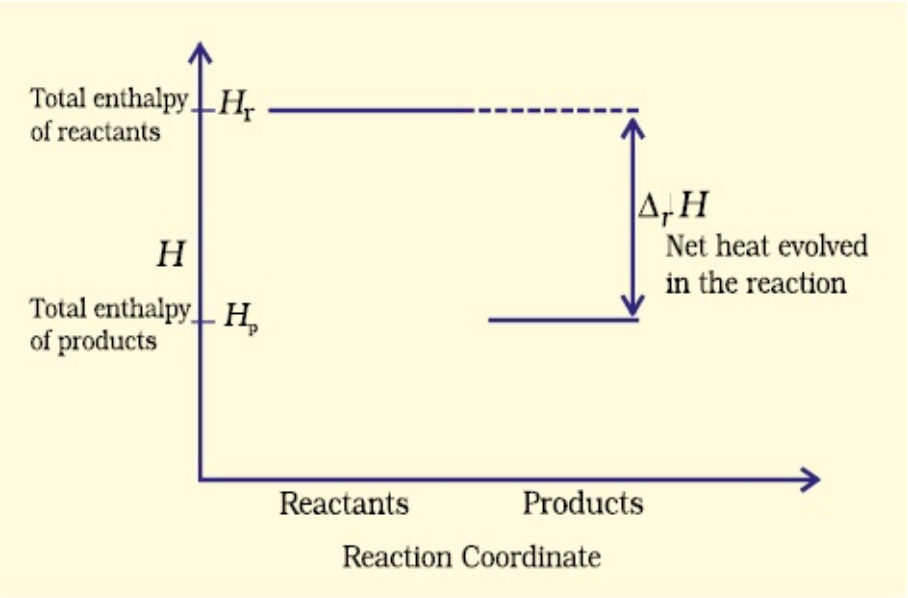


Fig. 6.10 (a) Enthalpy diagram for exothermic reactions

These reactions though endothermic, are spontaneous. The increase in enthalpy may be represented on an enthalpy diagram as shown in Fig. 6.10(b).

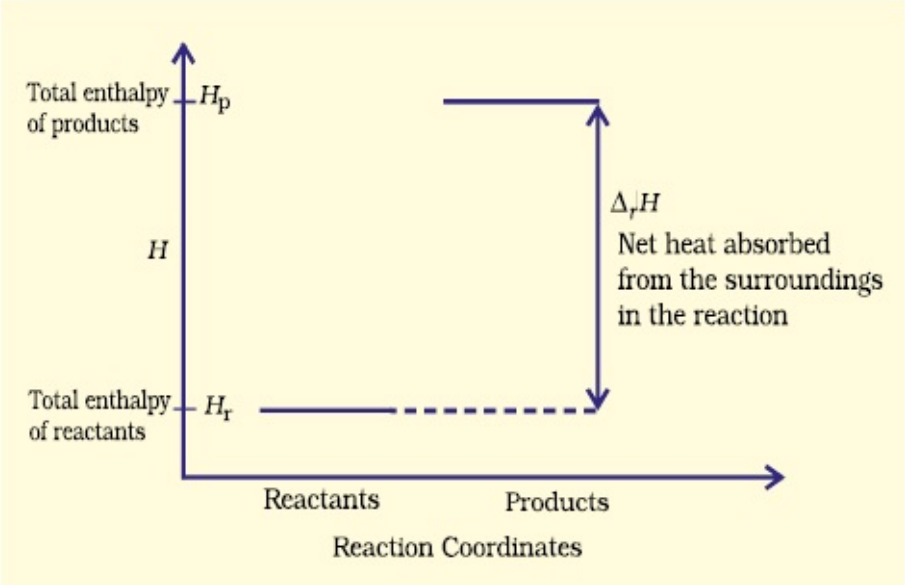


Fig. 6.10 (b) Enthalpy diagram for endothermic reactions

Therefore, it becomes obvious that while decrease in enthalpy may be a contributory factor for spontaneity, but it is not true for all cases.

(b) Entropy and Spontaneity

Then, what drives the spontaneous process in a given direction ? Let us examine such a case in which $\Delta H = 0$ i.e., there is no change in enthalpy, but still the process is spontaneous.

Let us consider diffusion of two gases into each other in a closed container which is isolated from the surroundings as shown in Fig. 6.11.

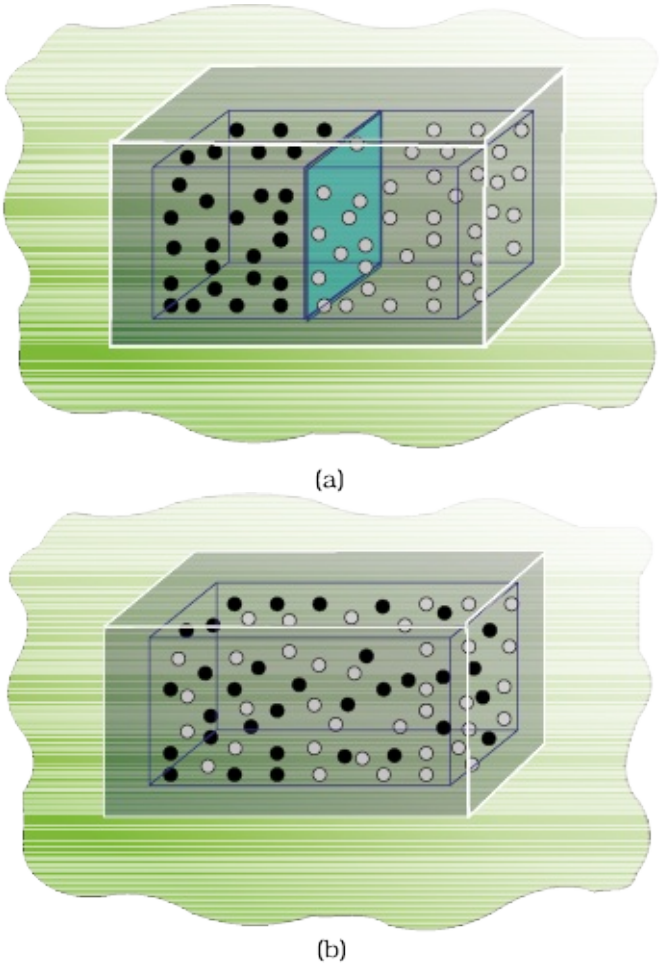
The two gases, say, gas A and gas B are represented by black dots and white dots respectively and separated by a movable partition [Fig. 6.11 (a)]. When the partition is withdrawn [Fig.6.11(b)], the gases begin to diffuse into each other and after a period of time, diffusion will be complete.

Let us examine the process. Before partition, if we were to pick up the gas molecules from left container, we would be sure that these will be molecules of gas A and similarly if we were to pick up the gas molecules from right container, we would be sure that these will be molecules of gas

B. But, if we were to pick up molecules from container when partition is removed, we are not sure whether the molecules picked are of gas A or gas B. We say that the system has become less predictable or more chaotic.

We may now formulate another postulate: in an isolated system, there is always a tendency for the systems' energy to become more disordered or chaotic and this could be a criterion for spontaneous change !

Fig. 6.11 Diffusion of two gases



At this point, we introduce another thermodynamic function, **entropy** denoted as S. The above mentioned disorder is the manifestation of entropy. To form a mental picture, one can think of entropy as a measure of the degree of randomness or disorder in the system. The greater the disorder in an isolated system, the higher is the entropy. As far as a

chemical reaction is concerned, this entropy change can be attributed to rearrangement of atoms or ions from one pattern in the reactants to another (in the products). If the structure of the products is very much disordered than that of the reactants, there will be a resultant increase in entropy. The change in entropy accompanying a chemical reaction may be estimated qualitatively by a consideration of the structures of the species taking part in the reaction. Decrease of regularity in structure would mean increase in entropy. For a given substance, the crystalline solid state is the state of lowest entropy (most ordered), The gaseous state is state of highest entropy.

Now let us try to quantify entropy. One way to calculate the degree of disorder or chaotic distribution of energy among molecules would be through statistical method which is beyond the scope of this treatment. Other way would be to relate this process to the heat involved in a process which would make entropy a thermodynamic concept. Entropy, like any other thermodynamic property such as internal energy U and enthalpy H is a state function and ΔS is independent of path.

Whenever heat is added to the system, it increases molecular motions causing increased randomness in the system. Thus **heat (q) has randomising influence** on the system. Can we then equate ΔS with q ? Wait ! Experience suggests us that the distribution of heat also depends on the temperature at which heat is added to the system. A system at higher temperature has greater randomness in it than one at lower temperature. Thus, **temperature is the measure of average chaotic motion of particles in the system.** Heat added to a system at lower temperature causes greater randomness than when the same quantity of heat is added to it at higher temperature. This suggests that the entropy change is inversely proportional to the temperature. $^{\Delta}S$ is related with q and T for a reversible reaction as :

$$\Delta S = \frac{q_{rev}}{T} \qquad (6.18)$$

The total entropy change (ΔS_{total}) for the system and surroundings of a spontaneous process is given by

$$\Delta S_{total} = \Delta S_{system} + \Delta S_{surr} > 0 \qquad (6.19)$$

When a system is in equilibrium, the entropy is maximum, and the change in entropy, $\Delta S = 0$.

We can say that entropy for a spontaneous process increases till it reaches maximum and at equilibrium the change in entropy is zero. Since entropy is a state property, we can calculate the change in entropy of a reversible process by

$$\Delta S_{sys} = \frac{q_{sys,rev}}{T}$$

We find that both for reversible and irreversible expansion for an ideal gas, under isothermal conditions, $\Delta U = 0$, but ΔS_{total} i.e., $\Delta S_{sys} + \Delta surr$ is not zero for irreversible process. Thus, ΔU does not discriminate between reversible and irreversible process, whereas ΔS does.

Problem 6.10

Predict in which of the following, entropy increases/decreases :

(i) A liquid crystallizes into a solid.

(ii) Temperature of a crystalline solid is raised from 0 K to 115 K.

(iii) $2NaHCO_3(s) \rightarrow Na_2CO_3(s) + CO_2(g) + H_2O(g)$

(iv) $H_2(g) \rightarrow 2H(g)$

Solution

(i) After freezing, the molecules attain an ordered state and therefore, entropy decreases.

(ii) At 0 K, the contituent particles are static and entropy is minimum. If temperature is raised

to 115 K, these begin to move and oscillate about their equilibrium positions in the lattice and system becomes more disordered, therefore entropy increases.

(iii) Reactant, NaHCO3 is a solid and it has low entropy. Among products there are one solid and two gases. Therefore, the products represent a condition of higher entropy.

(iv) Here one molecule gives two atoms i.e., number of particles increases leading to more disordered state. Two moles of H atoms have higher entropy than one mole of dihydrogen molecule.

Problem 6.11

For oxidation of iron,

$$4Fe(s)+3O_2(g)\rightarrow 2Fe_2O_3(s)$$

entropy change is – 549.4 $JK^{-1}mol^{-1}$at 298 K. Inspite of negative entropy change of this reaction, why is the reaction spontaneous?

($\Delta_r H^{\ominus}$for this reaction is -1648×10^3 J mol^{-1})

Solution

One decides the spontaneity of a reaction by considering

$\Delta S_{total}\left(\Delta S_{sys}+\Delta S_{surr}\right)$. For calculating ΔS_{surr}, we have to consider the heat absorbed by the surroundings which is equal to $-\Delta_r H^{\ominus}$. At temperature T, entropy change of the surroundings is

$$\Delta S_{surr}=-\frac{\Delta_r H^{\ominus}}{T}\ (\text{at constant pressure})$$

$$=-\frac{\left(-1648\times10^3\ \text{J mol}^{-1}\right)}{298\ \text{K}}$$

$= 5530\ JK^{-1}mol^{-1}$

Thus, total entropy change for this reaction

$$\Delta_r S_{total}=5530 JK^{-1}mol^{-1}+\left(-549.4 JK^{-1}mol^{-1}\right)$$

= 4980.6 JK–1 mol–1

This shows that the above reaction is spontaneous.

(c) Gibbs Energy and Spontaneity

We have seen that for a system, it is the total entropy change, ΔS_{total} which decides the spontaneity of the process. But most of the chemical reactions fall into the category of either closed systems or open systems. Therefore, for most of the chemical reactions there are changes in both enthalpy and entropy. It is clear from the discussion in previous sections that neither decrease in enthalpy nor increase in entropy alone can determine the direction of spontaneous change for these systems.

For this purpose, we define a new thermodynamic function the Gibbs energy or Gibbs function, G, as

$$G = H - TS \qquad (6.20)$$

Gibbs function, G is an extensive property and a state function.

The change in Gibbs energy for the system, ΔG_{sys} can be written as

$$\Delta G_{sys} = \Delta H_{sys} - T\Delta S_{sys} - S_{sys}\Delta T$$

At constant temperature, $\Delta T = 0$

$$\therefore \Delta G_{sys} = \Delta H_{sys} - T\Delta S_{sys}$$

Usually the subscript 'system' is dropped and we simply write this equation as

$$\Delta G = \Delta H - T\Delta S \qquad (6.21)$$

Thus, Gibbs energy change = enthalpy change – temperature × entropy change, and is referred to as the Gibbs equation, one of the most important equations in chemistry. Here, we have considered both terms together for spontaneity: energy (in terms of ΔH) and entropy (ΔS, a measure of disorder) as indicated earlier. Dimensionally if we analyse, we

find that ΔG has units of energy because, both ΔH and the $T\Delta S$ are energy terms, since $T\Delta S = (K)\ (J/K) = J$.

Now let us consider how ΔG is related to reaction spontaneity.

We know,

$\Delta S_{total} = \Delta S_{sys} + \Delta S_{surr}$

If the system is in thermal equilibrium with the surrounding, then the temperature of the surrounding is same as that of the system. Also, increase in enthalpy of the surrounding is equal to decrease in the enthalpy of the system.

Therefore, entropy change of surroundings,

$$\Delta S_{surr} = \frac{\Delta H_{surr}}{T} = -\frac{\Delta H_{sys}}{T}$$

$$\Delta S_{total} = \Delta S_{sys} + \left(-\frac{\Delta H_{sys}}{T}\right)$$

Rearranging the above equation:

$$T\Delta S_{total} = T\Delta S_{sys} - \Delta H_{sys}$$

For spontaneous process, $\Delta S_{total} > 0$, so

$$T\Delta S_{sys} - \Delta H_{sys} > O$$

$$\Rightarrow -\left(\Delta H_{sys} - T\Delta S_{sys}\right) > 0$$

Using equation 6.21, the above equation can be written as

$$-\Delta G > O$$

$$\Delta G = \Delta H - T\Delta S < 0 \qquad (6.22)$$

ΔH_{sys} is the enthalpy change of a reaction, $T\Delta S_{sys}$ is the energy which is not available to do useful work. So ΔG is the net energy available to do useful work and is thus a measure of the ‘free energy’. For this reason, it is also known as the free energy of the reaction.

ΔG gives a criteria for spontaneity at constant pressure and temperature.

(i) If ΔG is negative (< 0), the process is spontaneous.

(ii) If ΔG is positive (> 0), the process is non spontaneous.

Note : If a reaction has a positive enthalpy change and positive entropy change, it can be spontaneous when $T\Delta S$ is large enough to outweigh ΔH. This can happen in two ways; (a) The positive entropy change of the system can be 'small' in which case T must be large. (b) The positive entropy change of the system can be 'large', in which case T may be small. The former is one of the reasons why reactions are often carried out at high temperature. Table 6.4 summarises the effect of temperature on spontaneity of reactions.

(d) Entropy and Second Law of Thermodynamics

We know that for an isolated system the change in energy remains constant. Therefore, increase in entropy in such systems is the natural direction of a spontaneous change. This, in fact is the second law of thermodynamics. Like first law of thermodynamics, second law can also be stated in several ways. The second law of thermodynamics explains why spontaneous exothermic reactions are so common. In exothermic reactions heat released by the reaction increases the disorder of the surroundings and overall entropy change is positive which makes the reaction spontaneous.

(e) Absolute Entropy and Third Law of Thermodynamics

Molecules of a substance may move in a straight line in any direction, they may spin like a top and the bonds in the molecules may stretch and compress. These motions of the molecule are called translational, rotational and vibrational motion respectively. When temperature of the system rises, these motions become more vigorous and entropy increases. On the other hand when temperature is lowered, the entropy decreases. The entropy of any pure crystalline substance approaches zero as the temperature approaches absolute zero. This is called third law of thermodynamics. This is so because there is perfect order in a crystal at absolute zero. The statement is confined to pure crystalline

solids because theoretical arguments and practical evidences have shown that entropy of solutions and super cooled liquids is not zero at 0 K. The importance of the third law lies in the fact that it permits the calculation of absolute values of entropy of pure substance from thermal data alone. For a pure substance, this can be done by summing $\frac{q_{rev}}{T}$ increments from 0 K to 298 K. Standard entropies can be used to calculate standard entropy changes by a Hess's law type of calculation.

6.7 Gibbs energy change and equilibrium

We have seen how a knowledge of the sign and magnitude of the free energy change of a chemical reaction allows:

(i) Prediction of the spontaneity of the chemical reaction.

(ii) Prediction of the useful work that could be extracted from it.

So far we have considered free energy changes in irreversible reactions. Let us now examine the free energy changes in reversible reactions.

'Reversible' under strict thermodynamic sense is a special way of carrying out a process such that system is at all times in perfect equilibrium with its surroundings. When applied to a chemical reaction, the term 'reversible' indicates that a given reaction can proceed in either direction simultaneously, so that a dynamic equilibrium is set up. This means that the reactions in both the directions should proceed with a decrease in free energy, which seems impossible. It is possible only if at equilibrium the free energy of the system is minimum. If it is not, the system would spontaneously change to configuration of lower free energy.

So, the criterion for equilibrium

$A + B \leftrightharpoons C + D$; is

$\Delta_r G = 0$

Gibbs energy for a reaction in which all reactants and products are in

standard state, $\Delta_r G^\ominus$ is related to the equilibrium constant of the reaction as follows:

$$0 = \Delta_r G^\ominus + RT \ln K$$

$$\text{or} \quad \Delta_r G^\ominus = -RT \ln K$$

$$\text{or} \quad \Delta_r G^\ominus = -2.303\, RT \log K \qquad (6.23)$$

We also know that

$$\Delta_r G^\ominus = \Delta_r H^\ominus - T\Delta_r S^\ominus = -RT \ln K \qquad (6.24)$$

For strongly endothermic reactions, the value of $\Delta_r H^\ominus$ may be large and positive. In such a case, value of K will be much smaller than 1 and the reaction is unlikely to form much product. In case of exothermic reactions, $\Delta_r H^\ominus$ is large and negative, and $\Delta_r G^\ominus$ is likely to be large and negative too. In such cases, K will be much larger than 1. We may expect strongly exothermic reactions to have a large K, and hence can go to near completion. $\Delta_r G^\ominus$ also depends upon $\Delta_r S^\ominus$, if the changes in the entropy of reaction is also taken into account, the value of K or extent of chemical reaction will also be affected, depending upon whether $\Delta_r S^\ominus$ is positive or negative.

Table 6.4 Effect of Temperature on Spontaneity of Reactions

$\Delta_r H^\ominus$	$\Delta_r S^\ominus$	$\Delta_r G^\ominus$	Description*
–	+	–	Reaction spontaneous at all temperatures
–	–	– (at low T)	Reaction spontaneous at low temperature
–	–	+ (at high T)	Reaction nonspontaneous at high temperature
+	+	+ (at low T)	Reaction nonspontaneous at low temperature
+	+	– (at high T)	Reaction spontaneous at high temperature
+	–	+ (at all T)	Reaction nonspontaneous at all temperatures

** The term low temperature and high temperature are relative. For a particular reaction, high temperature could even mean room temperature.*

Using equation (6.24),

(i) It is possible to obtain an estimate of $\Delta G^{\ominus}$ from the measurement of ΔH^{V} and $\Delta S^{\ominus}$, and then calculate K at any temperature for economic yields of the products.

(ii) If K is measured directly in the laboratory, value of $\Delta G^{\ominus}$ at any other temperature can be calculated.

Using equation (6.24),

Problem 6.12

Calculate $\Delta_r G^{\ominus}$ for conversion of oxygen to ozone, 3/2 O2(g) → O3(g) at 298 K. if K_p for this conversion is 2.47 × 10–29.

Solution

We know $\Delta_r G^{\ominus}$ = – 2.303 RT log K_p and

R = 8.314 JK–1 mol–1

Therefore, $\Delta_r G^{\ominus}$ =

– 2.303 (8.314 J K–1 mol–1) × (298 K) (log 2.47 × 10–29)

= 163000 J mol–1

= 163 kJ mol–1.

Problem 6.13

Find out the value of equilibrium constant for the following reaction at 298 K.

$$2NH_3(g) + CO_2(g) \rightleftharpoons NH_2CONH_2(aq) + H_2O(l)$$

Standard Gibbs energy change, $\Delta_r G^{\ominus}$ at the given temperature is –13.6 kJ mol–1.

Solution

$$\text{We know, } \log K = \frac{-\Delta_r G^{\ominus}}{2.303\,RT}$$

$$= \frac{\left(-13.6 \times 10^{3}\ \text{J mol}^{-1}\right)}{2.303\left(8.314\ \text{JK}^{-1}\ \text{mol}^{-1}\right)(298\,\text{K})}$$

Hence K = antilog 2.38 = 2.4 × 102.

Problem 6.14

At 60°C, dinitrogen tetroxide is 50 per cent dissociated. Calculate the standard free energy change at this temperature and at one atmosphere.

Solution

$N_2O_4(g) \rightleftharpoons 2NO_2(g)$

If N_2O_4 is 50% dissociated, the mole fraction of both the substances is given by

$$x_{N_2O_4} = \frac{1 - 0.5}{1 + 0.5} : x_{NO_2} = \frac{2 \times 0.5}{1 + 0.5}$$

$$p_{N_2O_4} = \frac{0.5}{1.5} \times 1 \text{ atm}, p_{NO_2} = \frac{1}{1.5} \times 1 \text{ atm.}$$

The equilibrium constant K_p is given by

$$K_p = \frac{(p_{NO_2})^2}{p_{N_2O_4}} = \frac{1.5}{(1.5)^2\ (0.5)}$$

$= 1.33$ atm.

Since

$\Delta_r G^\ominus = -RT \ln K_p$

$\Delta_r G^\ominus = (-8.314\ JK^{-1}mol^{-1}) \times (333\ K) \times (2.303) \times (0.1239)$

$= -763.8\ kJ\ mol^{-1}$

Summary

Thermodynamics deals with energy changes in chemical or physical processes and enables us to study these changes quantitatively and to make useful predictions. For these purposes, we

divide the universe into the system and the surroundings. Chemical or physical processes lead to evolution or absorption of heat (q), part of which may be converted into work (w). These quantities are related through the **first law of thermodynamics** via $\Delta U = q + w$. ΔU, change in internal energy, depends on initial and final states only and is a state function, whereas q and w depend on the path and are not the state functions. We follow sign conventions of q and w by giving the positive sign to these quantities when these are added to the system. We can measure the transfer of heat from one system to another which causes the change in temperature. The magnitude of rise in temperature depends on the heat capacity (C) of a substance. Therefore, heat absorbed or evolved is $q = C\Delta T$. Work can be measured by $w = -p_{ex}\Delta V$, in case of expansion of gases. Under reversible process, we can put $p_{ex} = p$ for infinitesimal changes in the volume making $w_{rev} = -p\,dV$. In this condition, we can use gas equation, $pV = nRT$.

At constant volume, $w = 0$, then $\Delta U = q_V$, heat transfer at constant volume. But in study of chemical reactions, we usually have constant pressure. We define another state function **enthalpy**. Enthalpy change, $\Delta H = \Delta U + \Delta n_g RT$, can be found directly from the heat changes at constant pressure, $\Delta H = q_p$.

There are varieties of enthalpy changes. Changes of phase such as melting, vaporization and sublimation usually occur at constant temperature and can be characterized by enthalpy changes which are always positive. Enthalpy of formation, combustion and other enthalpy changes can be calculated using **Hess's law**. Enthalpy change for chemical reactions can be determined by

$$\Delta_r H = \sum_f \left(a_i \Delta_f H_{\text{products}}\right) - \sum_i \left(b_i \Delta_f H_{\text{reactions}}\right)$$

and in gaseous state by

$\Delta_r H0$ = Σ bond enthalpies of the reactants – Σ bond enthalpies of the products

First law of thermodynamics does not guide us about the direction of chemical reactions i.e., what is the driving force of a chemical reaction. For isolated systems,

$\Delta U = 0$. We define another state function, S, **entropy** for this purpose. **Entropy** is a measure of disorder or randomness. For a spontaneous change, total entropy change is positive. Therefore,

for an isolated system, $\Delta U = 0$, $\Delta S > 0$, so entropy change distinguishes a spontaneous change, while energy change does not. Entropy changes can be measured by the equation

$\Delta S = \frac{q_{rev}}{T}$ for a reversible process. $\frac{q_{rev}}{T}$ is independent of path.

Chemical reactions are generally carried at constant pressure, so we define another state function **Gibbs energy**, G, which is related to entropy and enthalpy changes of the system by the equation:

$\Delta_r G = \Delta_r H - T \Delta_r S$

For a spontaneous change, $\Delta G_{sys} < 0$ and at equilibrium, $\Delta G_{sys} = 0$.

Standard Gibbs energy change is related to equilibrium constant by

$\Delta_r G0 = - RT \ln K$.

K can be calculated from this equation, if we know $\Delta_r G0$ which can be found from $\Delta_r G^\ominus = \Delta_r H^\ominus - T\Delta_r S^\ominus$. Temperature is an important factor in the equation. Many reactions which are non-spontaneous at low temperature, are made spontaneous at high temperature for systems having positive entropy of reaction.

Exercises

6.1 Choose the correct answer. A thermodynamic state function is a quantity

(i) used to determine heat changes

(ii) whose value is independent of path

(iii) used to determine pressure volume work

(iv) whose value depends on temperature only.

6.2 For the process to occur under adiabatic conditions, the correct condition is:

(i) $\Delta T = 0$

(ii) $\Delta p = 0$

(iii) $q = 0$

(iv) $w = 0$

6.3 The enthalpies of all elements in their standard states are:

(i) unity

(ii) zero

(iii) < 0

(iv) different for each element

6.4 $\Delta U^0$of combustion of methane is – X kJ mol–1. The value of ΔH^0 is

(i) = ΔU^0

(ii) > ΔU^0

(iii) < ΔU^0

(iv) = 0

6.5 The enthalpy of combustion of methane, graphite and dihydrogen at 298 K are, –890.3 kJ mol–1 –393.5 kJ mol–1, and –285.8 kJ mol–1 respectively. Enthalpy of formation of $CH_4(g)$ will be

(i) –74.8 kJ mol–1

(ii) –52.27 kJ mol–1

(iii) +74.8 kJ mol–1

(iv) +52.26 kJ mol–1.

6.6 A reaction, A + B → C + D + q is found to have a positive entropy change. The reaction will be

(i) possible at high temperature

(ii) possible only at low temperature

(iii) not possible at any temperature

(v) possible at any temperature

6.7 In a process, 701 J of heat is absorbed by a system and 394 J of work is done by the system. What is the change in internal energy for the process?

6.8 The reaction of cyanamide, NH_2CN (s), with dioxygen was carried out in a bomb calorimeter, and ΔU was found to be –742.7 kJ mol–1 at 298 K. Calculate enthalpy change for the reaction at 298 K.

$NH_2CN(g) + \frac{3}{2} O_2(g) \rightarrow N_2(g) + CO_2(g) + H_2O(l)$

6.9 Calculate the number of kJ of heat necessary to raise the temperature of

60.0 g of aluminium from 35°C to 55°C. Molar heat capacity of Al is 24 J mol–1 K–1.

6.10 Calculate the enthalpy change on freezing of 1.0 mol of water at10.0°C to ice at –10.0°C. $\Delta_{fus}H$ = 6.03 kJ mol–1 at 0°C.

C_p [$H_2O(l)$] = 75.3 J mol–1 K–1

C_p [$H_2O(s)$] = 36.8 J mol–1 K–1

6.11 Enthalpy of combustion of carbon to CO_2 is –393.5 kJ mol–1. Calculate the heat released upon formation of 35.2 g of CO_2 from carbon and dioxygen gas.

6.12 Enthalpies of formation of CO(g), CO_2(g), N_2O(g) and N_2O_4(g) are –110, – 393, 81 and 9.7 kJ mol–1 respectively. Find the value of Δ_rH for the reaction:

$N_2O_4(g) + 3CO(g) \rightarrow N_2O(g) + 3CO_2(g)$

6.13 Given

$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$; Δ_rH0 = –92.4 kJ mol–1

What is the standard enthalpy of formation of NH_3 gas?

6.14 Calculate the standard enthalpy of formation of $CH_3OH(l)$ from the following data:

$CH_3OH\ (l) + \frac{3}{2} O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$; Δ_rH0 = –726 kJ mol–1

$C(graphite) + O_2(g) \rightarrow CO_2(g)$; Δ_cH0 = –393 kJ mol–1

$H_2(g) + \frac{1}{2} O_2(g) \rightarrow H_2O(l)$; $\Delta_f H0$ = –286 kJ mol–1.

6.15 Calculate the enthalpy change for the process

$CCl_4(g) \rightarrow C(g) + 4\ Cl(g)$

and calculate bond enthalpy of C – Cl in $CCl_4(g)$.

$\Delta_{vap}H0(CCl_4) = 30.5$ kJ mol–1.

$\Delta_fH0\ (CCl_4) = –135.5$ kJ mol–1.

$\Delta_aH0\ (C) = 715.0$ kJ mol–1 , where Δ_aH0 is enthalpy of atomisation

$\Delta_aH0\ (Cl_2) = 242$ kJ mol–1

6.16 For an isolated system, $\Delta U = 0$, what will be ΔS ?

6.17 For the reaction at 298 K,

$2A + B \rightarrow C$

$\Delta H = 400$ kJ mol–1 and $\Delta S = 0.2$ kJ K–1 mol–1

At what temperature will the reaction become spontaneous considering ΔH and ΔS to be constant over the temperature range.

6.18 For the reaction,

$2\ Cl(g) \rightarrow Cl_2(g)$, what are the signs of ΔH and ΔS ?

6.19 For the reaction

$2\ A(g) + B(g) \rightarrow 2D(g)$

$\Delta U\ 0 = –10.5$ kJ and $\Delta S0 = –44.1$ JK–1.

Calculate $\Delta G0$ for the reaction, and predict whether the reaction may occur spontaneously.

6.20 The equilibrium constant for a reaction is 10. What will be the value of $\Delta G0$?

R = 8.314 JK–1 mol–1, T = 300 K.

6.21 Comment on the thermodynamic stability of NO(g), given

$\frac{1}{2}\ N_2(g) + \frac{1}{2} O_2(g) \rightarrow NO(g)$; $\Delta_rH0 = 90$ kJ mol–1

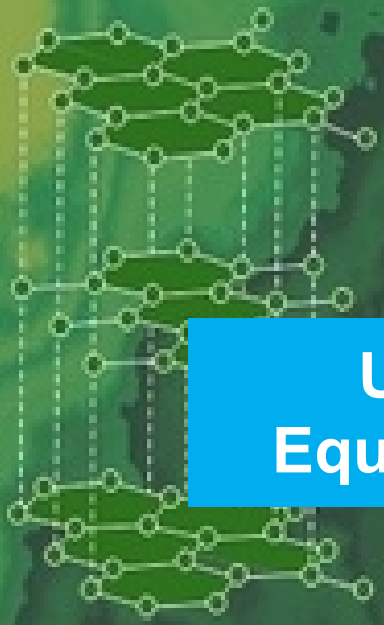
$NO(g) + \frac{1}{2} O_2(g) \rightarrow NO_2(g)$: $\Delta_rH0 = –74$ kJ mol–1

6.22 Calculate the entropy change in surroundings when 1.00 mol of $H_2O(l)$ is formed under standard conditions. $\Delta_f H^0 = -286$ kJ mol–1.

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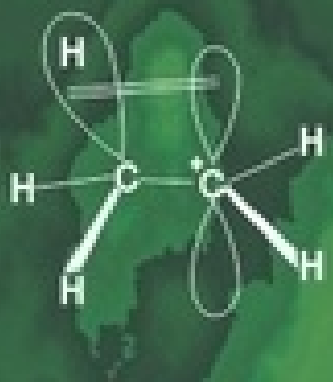
Textbook for Class XI



Unit 7
Equilibrium

Chemistry

Part I



11082CH07

Unit 7

Equilibrium

Objectives

After studying this unit you will be able to

- identify dynamic nature of equilibrium involved in physical and chemical processes;
- state the law of equilibrium;
- explain characteristics of equilibria involved in physical and chemical processes;
- write expressions for equilibrium constants;
- establish a relationship between Kp and Kc;
- explain various factors that affect the equilibrium state of a reaction;
- classify substances as acids or bases according to Arrhenius, Bronsted-Lowry and Lewis concepts;
- classify acids and bases as weak or strong in terms of their ionization constants;
- explain the dependence of degree of ionization on concentration of the electrolyte and that of the common ion;
- describe pH scale for representing hydrogen ion concentration;
- explain ionisation of water and its duel role as acid and base;
- describe ionic product (Kw) and pKw for water;
- appreciate use of buffer solutions;
- calculate solubility product constant.

Chemical equilibria are important in numerous biological and environmental processes. For example, equilibria involving O_2 molecules and the protein hemoglobin play a crucial role in the transport and delivery of O_2 from our lungs to our muscles. Similar equilibria involving CO molecules and hemoglobin account for the toxicity of CO.

When a liquid evaporates in a closed container, molecules with relatively higher kinetic energy escape the liquid surface into the vapour phase and number of liquid molecules from the vapour phase strike the liquid surface and are retained in the liquid phase. It gives rise to a constant vapour pressure because of an equilibrium in which the number of molecules leaving the liquid equals the number returning to liquid from the vapour. We say that the system has reached **equilibrium state** at this stage. However, this is not static equilibrium and there is a lot of activity at the boundary between the liquid and the vapour. Thus, at equilibrium, the rate of evaporation is equal to the rate of condensation. It may be represented by

$H_2O\ (l) \leftrightharpoons H_2O\ (vap)$

The double half arrows indicate that the processes in both the directions are going on simultaneously. The mixture of reactants and products in the equilibrium state is called an **equilibrium mixture**.

Equilibrium can be established for both physical processes and chemical reactions. The reaction may be fast or slow depending on the experimental conditions and the nature of the reactants. When the reactants in a closed vessel at a particular temperature react to give products, the concentrations of the reactants keep on decreasing, while those of products keep on increasing for some time after which there is no change in the concentrations of either of the reactants or products. This stage of the system is the **dynamic equilibrium** and the rates of the

forward and reverse reactions become equal. It is due to this dynamic equilibrium stage that there is no change in the concentrations of various species in the reaction mixture. Based on the extent to which the reactions proceed to reach the state of **chemical equilibrium,** these may be classified in three groups.

(i) The reactions that proceed nearly to completion and only negligible concentrations of the reactants are left. In some cases, it may not be even possible to detect these experimentally.

(ii) The reactions in which only small amounts of products are formed and most of the reactants remain unchanged at equilibrium stage.

(iii) The reactions in which the concentrations of the reactants and products are comparable, when the system is in equilibrium.

The extent of a reaction in equilibrium varies with the experimental conditions such as concentrations of reactants, temperature, etc. Optimisation of the operational conditions is very important in industry and laboratory so that equilibrium is favorable in the direction of the desired product. Some important aspects of equilibrium involving physical and chemical processes are dealt in this unit along with the equilibrium involving ions in aqueous solutions which is called as **ionic equilibrium**.

7.1 EQUILIBRIUM IN PHYSICAL PROCESSES

The characteristics of system at equilibrium are better understood if we examine some physical processes. The most familiar examples are **phase transformation processes**, e.g.,

solid $\rightleftharpoons$ liquid

liquid $\rightleftharpoons$ gas

solid $\rightleftharpoons$ gas

7.1.1 Solid-Liquid Equilibrium

Ice and water kept in a perfectly insulated thermos flask (no exchange of heat between its contents and the surroundings) at 273K and the atmospheric pressure are in equilibrium state and the system shows

interesting characteristic features. We observe that the mass of ice and water do not change with time and the temperature remains constant. However, the equilibrium is not static. The intense activity can be noticed at the boundary between ice and water. Molecules from the liquid water collide against ice and adhere to it and some molecules of ice escape into liquid phase. There is no change of mass of ice and water, as the rates of transfer of molecules from ice into water and of reverse transfer from water into ice are equal at atmospheric pressure and 273 K.

It is obvious that ice and water are in equilibrium only at particular temperature and pressure. For any pure substance at atmospheric pressure, the temperature at which the solid and liquid phases are at equilibrium is called the normal melting point or normal freezing point of the substance. The system here is in dynamic equilibrium and we can infer the following:

(i) Both the opposing processes occur simultaneously.

(ii) Both the processes occur at the same rate so that the amount of ice and water remains constant.

7.1.2 Liquid-Vapour Equilibrium

This equilibrium can be better understood if we consider the example of a transparent box carrying a U-tube with mercury (manometer). Drying agent like anhydrous calcium chloride (or phosphorus penta-oxide) is placed for a few hours in the box. After removing the drying agent by tilting the box on one side, a watch glass (or petri dish) containing water is quickly placed inside the box. It will be observed that the mercury level in the right limb of the manometer slowly increases and finally attains a constant value, that is, the pressure inside the box increases and reaches a constant value. Also the volume of water in the watch glass decreases (Fig. 7.1). Initially there was no water vapour (or very less) inside the box. As water evaporated the pressure in the box increased due to addition of water molecules into the gaseous phase inside the box.

The rate of evaporation is constant. However, the rate of increase in pressure decreases with time due to condensation of vapour into water. Finally it leads to an equilibrium condition when there is no net evaporation. This implies that the number of water molecules from the gaseous state into the liquid state also increases till the equilibrium is attained i.e.,

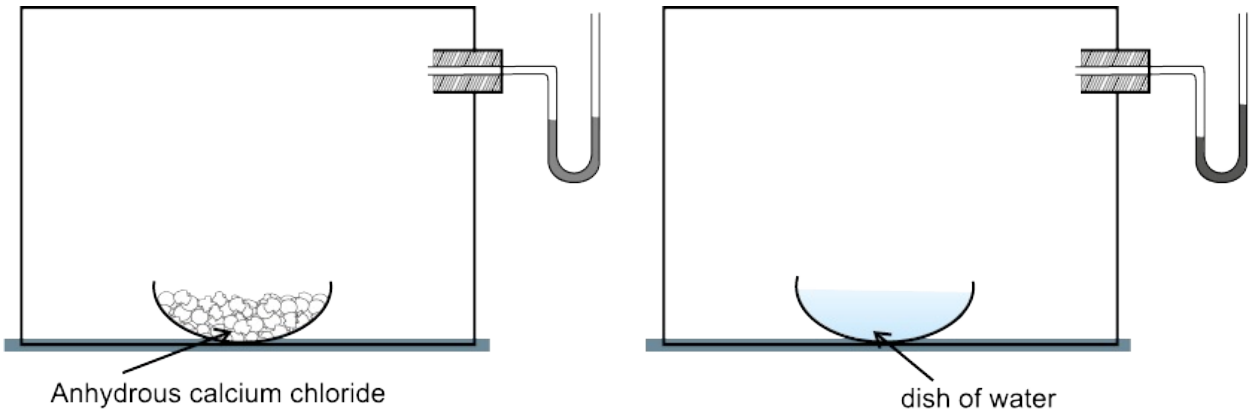


Fig.7.1 Measuring equilibrium vapour pressure of water at a constant temperature

rate of evaporation= rate of condensation

$H_2O(l) \rightleftharpoons H_2O$ (vap)

At equilibrium the pressure exerted by the water molecules at a given temperature remains constant and is called the equilibrium vapour pressure of water (or just vapour pressure of water); vapour pressure of water increases with temperature. If the above experiment is repeated with methyl alcohol, acetone and ether, it is observed that different liquids have different equilibrium vapour pressures at the same temperature, and the liquid which has a higher vapour pressure is more volatile and has a lower boiling point.

If we expose three watch glasses containing separately 1mL each of acetone, ethyl alcohol, and water to atmosphere and repeat the experiment with different volumes of the liquids in a warmer room, it is observed that in all such cases the liquid eventually disappears and the

time taken for complete evaporation depends on (i) the nature of the liquid, (ii) the amount of the liquid and (iii) the temperature. When the watch glass is open to the atmosphere, the rate of evaporation remains constant but the molecules are dispersed into large volume of the room. As a consequence the rate of condensation from vapour to liquid state is much less than the rate of evaporation. These are open systems and it is not possible to reach equilibrium in an open system.

Water and water vapour are in equilibrium position at atmospheric pressure (1.013 bar) and at 100°C in a closed vessel. The boiling point of water is 100°C at 1.013 bar pressure. For any pure liquid at one atmospheric pressure (1.013 bar), the temperature at which the liquid and vapours are at equilibrium is called normal boiling point of the liquid. Boiling point of the liquid depends on the atmospheric pressure. It depends on the altitude of the place; at high altitude the boiling point decreases.

7.1.3 Solid – Vapour Equilibrium

Let us now consider the systems where solids sublime to vapour phase. If we place solid iodine in a closed vessel, after sometime the vessel gets filled up with violet vapour and the intensity of colour increases with time. After certain time the intensity of colour becomes constant and at this stage equilibrium is attained. Hence solid iodine sublimes to give iodine vapour and the iodine vapour condenses to give solid iodine. The equilibrium can be represented as,

$I_2(solid) \quad I_2$ (vapour)

Other examples showing this kind of equilibrium are,

Camphor (solid) ⇋ Camphor (vapour)

NH_4Cl (solid) ⇋ NH_4Cl (vapour)

7.1.4 Equilibrium Involving Dissolution of Solid or Gases in Liquids

Solids in liquids

We know from our experience that we can dissolve only a limited amount of salt or sugar in a given amount of water at room temperature. If we make a thick sugar syrup solution by dissolving sugar at a higher temperature, sugar crystals separate out if we cool the syrup to the room temperature. We call it a saturated solution when no more of solute can be dissolved in it at a given temperature. The concentration of the solute in a saturated solution depends upon the temperature. In a saturated solution, a dynamic equilibrium exits between the solute molecules in the solid state and in the solution:

Sugar (solution) Sugar (solid), and

the rate of dissolution of sugar = rate of crystallisation of sugar.

Equality of the two rates and dynamic nature of equilibrium has been confirmed with the help of radioactive sugar. If we drop some radioactive sugar into saturated solution of non-radioactive sugar, then after some time radioactivity is observed both in the solution and in the solid sugar. Initially there were no radioactive sugar molecules in the solution but due to dynamic nature of equilibrium, there is exchange between the radioactive and non-radioactive sugar molecules between the two phases. The ratio of the radioactive to non-radioactive molecules in the solution increases till it attains a constant value.

Gases in liquids

When a soda water bottle is opened, some of the carbon dioxide gas dissolved in it fizzes out rapidly. The phenomenon arises due to difference in solubility of carbon dioxide at different pressures. There is equilibrium between the molecules in the gaseous state and the molecules dissolved in the liquid under pressure i.e.,

CO_2 (gas) $\rightleftharpoons$ CO2 (in solution)

This equilibrium is governed by Henry's law, **which states that the mass of a gas dissolved in a given mass of a solvent at any temperature**

is proportional to the pressure of the gas above the solvent. This amount decreases with increase of temperature. The soda water bottle is sealed under pressure of gas when its solubility in water is high. As soon as the bottle is opened, some of the dissolved carbon dioxide gas escapes to reach a new equilibrium condition required for the lower pressure, namely its partial pressure in the atmosphere. This is how the soda water in bottle when left open to the air for some time, turns 'flat'. It can be generalised that:

(i) For solid $\rightleftharpoons$ liquid equilibrium, there is only one temperature (melting point) at

1 atm (1.013 bar) at which the two phases can coexist. If there is no exchange of heat with the surroundings, the mass of the two phases remains constant.

(ii) For liquid $\rightleftharpoons$ vapour equilibrium, the vapour pressure is constant at a given temperature.

(iii) For dissolution of solids in liquids, the solubility is constant at a given temperature.

(iv) For dissolution of gases in liquids, the concentration of a gas in liquid is proportional to the pressure (concentration) of the gas over the liquid. These observations are summarised in Table 7.1

Table 7.1 Some Features of Physical Equilibria

Process	Conclusion
Liquid $\rightleftharpoons$ Vapour H_2O (l) $\rightleftharpoons$ H_2O (g)	p_{H_2O} constant at given temperature
Solid $\rightleftharpoons$ Liquid H_2O (s) $\rightleftharpoons$ H_2O (l)	Melting point is fixed at constant pressure
Solute(s) $\rightleftharpoons$ Solute (solution) Sugar(s) $\rightleftharpoons$ Sugar (solution)	Concentration of solute in solution is constant at a given temperature
Gas(g) $\rightleftharpoons$ Gas (aq) CO_2(g) $\rightleftharpoons$ CO_2(aq)	[gas(aq)]/[gas(g)] is constant at a given temperature $[CO_2(aq)]/[CO_2(g)]$ is constant at a given temperature

7.1.5 General Characteristics of Equilibria Involving Physical Processes

For the physical processes discussed above, following characteristics are common to the system at equilibrium:

(i) Equilibrium is possible only in a closed system at a given temperature.

(ii) Both the opposing processes occur at the same rate and there is a dynamic but stable condition.

(iii) All measurable properties of the system remain constant.

(iv) When equilibrium is attained for a physical process, it is characterised by constant value of one of its parameters at a given temperature. Table 7.1 lists such quantities.

(v) The magnitude of such quantities at any stage indicates the extent to which the physical process has proceeded before reaching equilibrium.

7.2 EQUILIBRIUM IN CHEMICAL PROCESSES – DYNAMIC EQUILIBRIUM

Analogous to the physical systems chemical reactions also attain a state of equilibrium. These reactions can occur both in forward and backward directions. When the rates of the forward and reverse reactions become

equal, the concentrations of the reactants and the products remain constant. This is the stage of chemical equilibrium. This equilibrium is dynamic in nature as it consists of a forward reaction in which the reactants give product(s) and reverse reaction in which product(s) gives the original reactants.

For a better comprehension, let us consider a general case of a reversible reaction,

$A + B \rightleftharpoons C + D$

With passage of time, there is accumulation of the products C and D and depletion of the reactants A and B (Fig. 7.2). This leads to a decrease in the rate of forward reaction and an increase in he rate of the reverse reaction,

Eventually, the two reactions occur at the same rate and the system reaches a state of equilibrium.

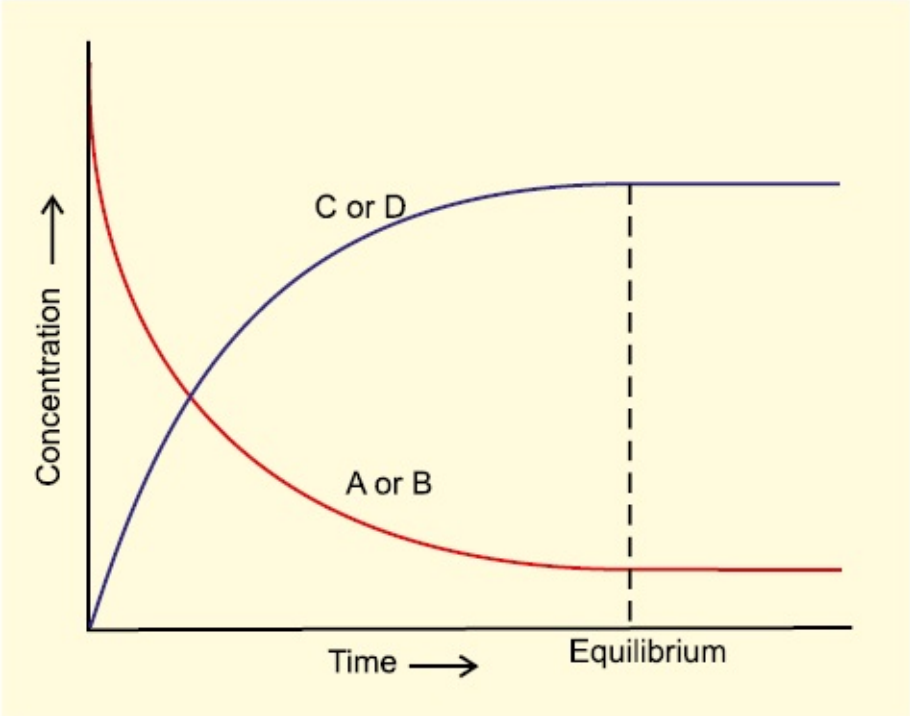


Fig. 7.2 Attainment of chemical equilibrium.

Similarly, the reaction can reach the state of equilibrium even if we start with only C and D; that is, no A and B being present initially, as the

equilibrium can be reached from either direction.

The dynamic nature of chemical equilibrium can be demonstrated in the synthesis of ammonia by Haber's process. In a series of experiments, Haber started with known amounts of dinitrogen and dihydrogen maintained at high temperature and pressure and at regular intervals determined the amount of ammonia present. He was successful in determining also the concentration of unreacted dihydrogen and dinitrogen. Fig. 7.4 (page 191) shows that after a certain time the composition of the mixture remains the same even though some of the reactants are still present. This constancy in composition indicates that the reaction has reached equilibrium. In order to understand the dynamic nature of the reaction, synthesis of ammonia is carried out with exactly the same starting conditions (of partial pressure and temperature) but using D_2 (deuterium) in place of H_2. The reaction mixtures starting either with H_2 or D_2 reach equilibrium with the same composition, except that D_2 and ND_3 are present instead of H_2 and NH_3. After equilibrium is attained, these two mixtures
(H_2, N_2, NH_3 and D_2, N_2, ND_3) are mixed together and left for a while. Later, when this mixture is analysed, it is found that the concentration of ammonia is just the same as before. However, when this mixture is analysed by a mass spectrometer, it is found that ammonia and all deuterium containing forms of ammonia (NH_3, NH_2D, NHD_2 and ND_3) and dihydrogen and its deutrated forms
(H_2, HD and D_2) are present. Thus one can conclude that scrambling of H and D atoms in the molecules must result from a continuation of the forward and reverse reactions in the mixture. If the reaction had simply stopped when they reached equilibrium, then there would have been no mixing of isotopes in this way.

Dynamic Equilibrium – A Student's Activity

Equilibrium whether in a physical or in a chemical system, is always of dynamic nature. This can be demonstrated by the use of radioactive isotopes. This is not feasible in a school laboratory. However this concept can be easily comprehended by performing the following activity. The activity can be performed in a group of 5 or 6 students.

Take two 100mL measuring cylinders (marked as 1 and 2) and two glass tubes each of 30 cm length. Diameter of the tubes may be same or different in the range of 3-5mm. Fill nearly half of the measuring cylinder-1 with coloured water (for this purpose add a crystal of potassium permanganate to water) and keep second cylinder (number 2) empty.

Put one tube in cylinder 1 and second in cylinder 2. Immerse one tube in cylinder 1, close its upper tip with a finger and transfer the coloured water contained in its lower portion to cylinder 2. Using second tube, kept in 2^{nd} cylinder, transfer the coloured water in a similar manner from cylinder 2 to cylinder 1. In this way keep on transferring coloured water using the two glass tubes from cylinder 1 to 2 and from 2 to 1 till you notice that the level of coloured water in both the cylinders becomes constant.

If you continue intertransferring coloured solution between the cylinders, there will not be any further change in the levels of coloured water in two cylinders. If we take analogy of 'level' of coloured water with 'concentration' of reactants and products in the two cylinders, we can say the process of transfer, which continues even after the constancy of level, is indicative of dynamic nature of the process. If we repeat the experiment taking two tubes of different diameters we find that at equilibrium the level of coloured water in two cylinders is different. How far diameters are responsible for change in levels in two cylinders? Empty cylinder (2) is an indicator of no product in it at the beginning.

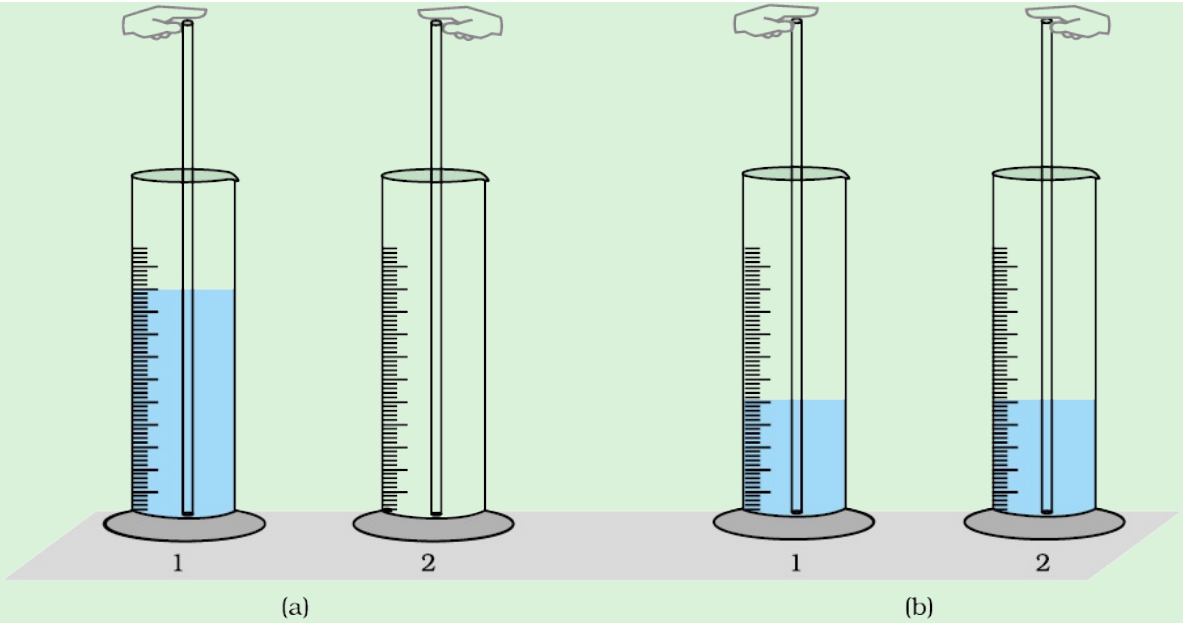


Fig.7.3 Demonstrating dynamic nature of equilibrium. (a) initial stage (b) final stage after the equilibrium is attained.

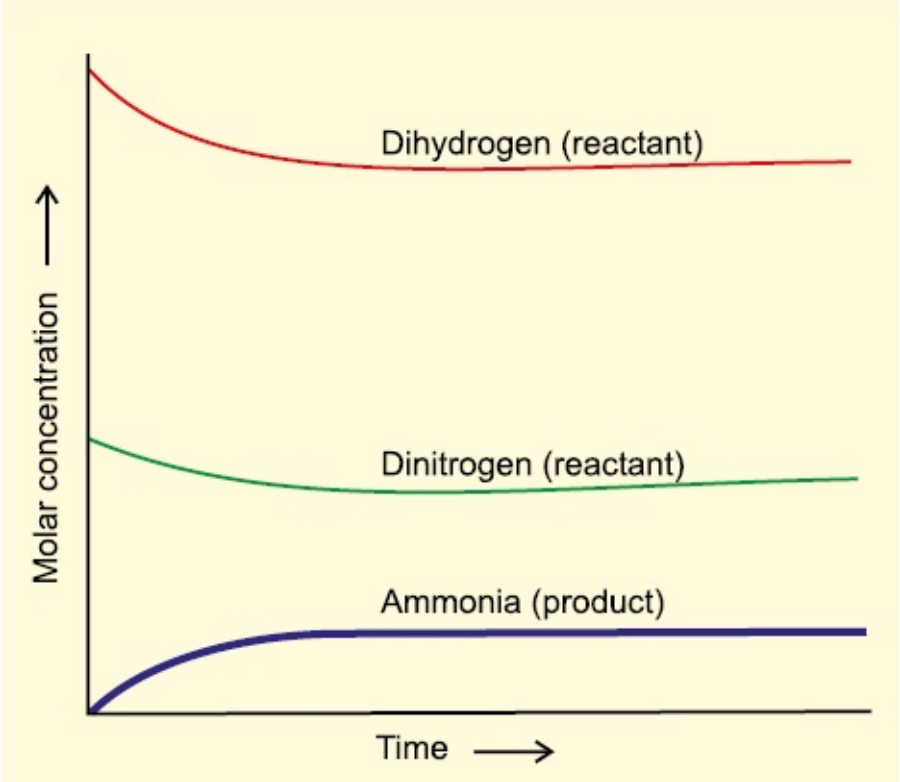


Fig 7.4 Depiction of equilibrium for the reaction

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

Use of isotope (deuterium) in the formation of ammonia clearly indicates that **chemical reactions reach a state of dynamic equilibrium in which the rates of forward and reverse reactions are equal and there is no net change in composition.**

Equilibrium can be attained from both sides, whether we start reaction by taking, $H_2(g)$ and $N_2(g)$ and get $NH_3(g)$ or by taking $NH_3(g)$ and decomposing it into $N_2(g)$ and $H_2(g)$.

$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

$2NH_3(g) \rightleftharpoons N_2(g) + 3H_2(g)$

Similarly let us consider the reaction,

$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$. If we start with equal initial concentration of H_2 and I_2, the reaction proceeds in the forward direction and the concentration of H_2 and I_2 decreases while that of HI increases, until all of these become constant at equilibrium (Fig. 7.5). We can also start with HI alone and make the reaction to proceed in the reverse direction; the concentration of HI will decrease and concentration of H_2 and I_2 will increase until they all become constant when equilibrium is reached (Fig.7.5). If total number of H and I atoms are same in a given volume, the same equilibrium mixture is obtained whether we start it from pure reactants or pure product.

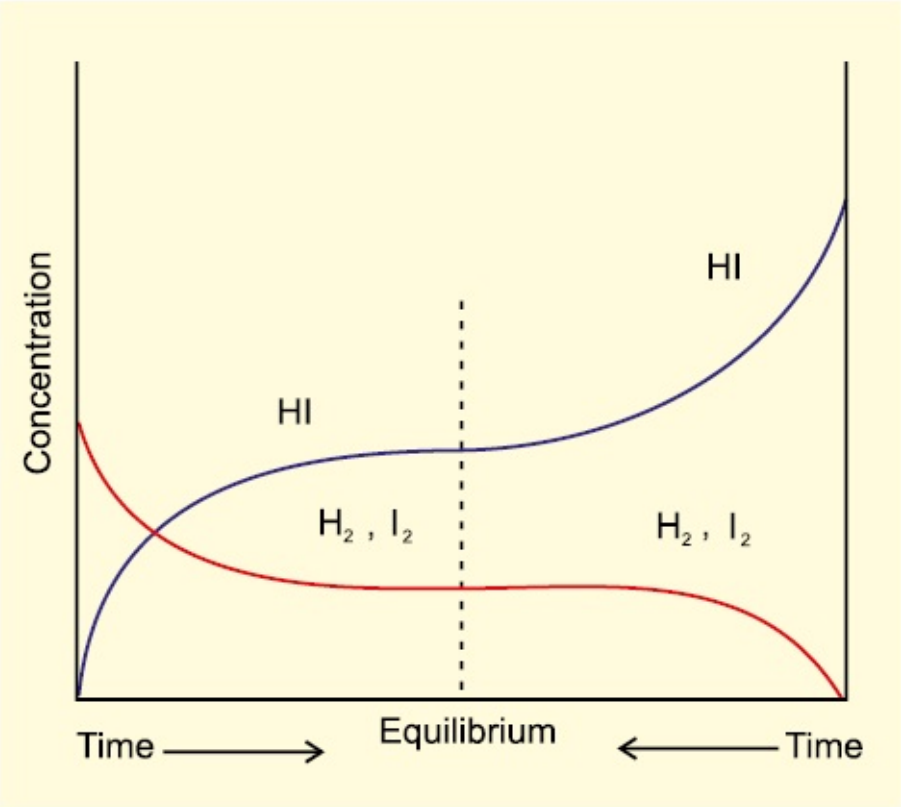


Fig.7.5 Chemical equilibrium in the reaction $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ can be attained from either direction

7.3 LAW OF CHEMICAL EQUILIBRIUM AND EQUILIBRIUM CONSTANT

A mixture of reactants and products in the equilibrium state is called an equilibrium mixture. In this section we shall address a number of important questions about the composition of equilibrium mixtures: What is the relationship between the concentrations of reactants and products in an equilibrium mixture? How can we determine equilibrium concentrations from initial concentrations? What factors can be exploited to alter the composition of an equilibrium mixture? The last question in particular is important when choosing conditions for synthesis of industrial chemicals such as H_2, NH_3, CaO etc.

To answer these questions, let us consider a general reversible reaction:

$A + B \rightleftharpoons C + D$

where A and B are the reactants, C and D are the products in the balanced chemical equation. On the basis of experimental studies of many reversible reactions, the Norwegian chemists Cato Maximillian Guldberg and Peter Waage proposed in 1864 that the concentrations in an equilibrium mixture are related by the following **equilibrium equation,**

$$K_c = \frac{[C][D]}{[A][B]} \quad (7.1)$$

where Kc is the equilibrium constant and the expression on the right side is called the equilibrium constant expression. The equilibrium equation is also known as the law of mass action because in the early days of chemistry, concentration was called “active mass”. In order to appreciate their work better, let us consider reaction between gaseous H_2 and I_2 carried out in a sealed vessel at 731K.

$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$

1 mol 1 mol 2 mol

Six sets of experiments with varying initial conditions were performed, starting with only gaseous H2 and I2 in a sealed reaction vessel in first four experiments (1, 2, 3 and 4) and only HI in other two experiments (5 and 6). Experiment 1, 2, 3 and 4 were performed taking different concentrations of H2 and / or I2, and with time it was observed that intensity of the purple colour remained constant and equilibrium was attained. Similarly, for experiments 5 and 6, the equilibrium was attained from the opposite direction.

Data obtained from all six sets of experiments are given in Table 7.2.

It is evident from the experiments 1, 2, 3 and 4 that number of moles of dihydrogen reacted = number of moles of iodine reacted = ½ (number of moles of HI formed). Also, experiments 5 and 6 indicate that,

$[H_2(g)]_{eq} = [I_2(g)]_{eq}$

Knowing the above facts, in order to establish a relationship between

concentrations of the reactants and products, several combinations can be tried. Let us consider the simple expression,

$[HI(g)]_{eq} / [H_2(g)]_{eq} [I_2(g)]_{eq}$

It can be seen from Table 7.3 that if we put the equilibrium concentrations of the reactants and products, the above expression is far from constant. However, if we consider the expression,

$[HI(g)]^2_{eq} / [H_2(g)]_{eq} [I_2(g)]_{eq}$

we find that this expression gives constant value (as shown in Table 7.3) in all the six cases. It can be seen that in this expression the power of the concentration for reactants and products are actually the stoichiometric coefficients in the equation for the chemical reaction. Thus, for the reaction $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$, following equation 7.1, the equilibrium constant Kc is written as,

Table 7.2 Initial and Equilibrium Concentrations of H_2, I_2 and HI

Experiment number	Initial concentration/mol L^{-1}			Equilibrium concentration/mol L^{-1}		
	$[H_2(g)]$	$[I_2(g)]$	$[HI(g)]$	$[H_2(g)]$	$[I_2(g)]$	$[HI(g)]$
1	2.4×10^{-2}	1.38×10^{-2}	0	1.14×10^{-2}	0.12×10^{-2}	2.52×10^{-2}
2	2.4×10^{-2}	1.68×10^{-2}	0	0.92×10^{-2}	0.20×10^{-2}	2.96×10^{-2}
3	2.44×10^{-2}	1.98×10^{-2}	0	0.77×10^{-2}	0.31×10^{-2}	3.34×10^{-2}
4	2.46×10^{-2}	1.76×10^{-2}	0	0.92×10^{-2}	0.22×10^{-2}	3.08×10^{-2}
5	0	0	3.04×10^{-2}	0.345×10^{-2}	0.345×10^{-2}	2.35×10^{-2}
6	0	0	7.58×10^{-2}	0.86×10^{-2}	0.86×10^{-2}	5.86×10^{-2}

Table 7.3 Expression Involving the Equilibrium Concentration of Reactants $H_2(g) + I_2(g)$ $2HI(g)$

Experiments Number	$\frac{[HI(g)]_{eq}}{[H_2(g)]_{eq}[I_2(g)]_{eq}}$	$\frac{[HI(g)]^2_{eq}}{[H_2(g)]_{eq}[I_2(g)]_{eq}}$
1	1840	46.4
2	1610	47.6
3	1400	46.7
4	1520	46.9
5	1970	46.4
6	790	46.4

$Kc = [HI(g)]_{eq}^2 / [H_2(g)]_{eq} [I_2(g)]_{eq}$ (7.2)

Generally the subscript 'eq' (used for equilibrium) is omitted from the concentration terms. It is taken for granted that the concentrations in the expression for Kc are equilibrium values. We, therefore, write,

$Kc = [HI(g)]^2 / [H_2(g)] [I_2(g)]$ (7.3)

The subscript 'c' indicates that Kc is expressed in concentrations of mol L^{-1}.

At a given temperature, the product of concentrations of the reaction products raised to the respective stoichiometric coefficient in the balanced chemical equation divided by the product of concentrations of the reactants raised to their individual stoichiometric coefficients has a constant value. This is known as the Equilibrium Law or Law of Chemical Equilibrium.

The equilibrium constant for a general reaction,

$a\ A + b\ B \rightleftharpoons c\ C + d\ D$

is expressed as,

$Kc = [C]^c[D]^d / [A]^a[B]^b$ (7.4)

where [A], [B], [C] and [D] are the equilibrium concentrations of the reactants and products.

Equilibrium constant for the reaction,
$4NH_3(g) + 5O_2(g) \rightleftharpoons 4NO(g) + 6H_2O(g)$ is written as

$Kc = [NO]^4[H_2O]^6 / [NH_3]^4 [O_2]^5$

Molar concentration of different species is indicated by enclosing these in square bracket and, as mentioned above, it is implied that these are equilibrium concentrations. While writing expression for equilibrium constant, symbol for phases (s, l, g) are generally ignored.
Let us write equilibrium constant for the reaction, $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ (7.5)

as, $Kc = [HI]^2 / [H_2] [I_2] = x$ (7.6)

The equilibrium constant for the reverse reaction, $2HI(g) \rightleftharpoons H_2(g) + I_2(g)$, at the same temperature is,

$K'c = [H_2] [I_2] / [HI]^2 = 1/ x = 1 / Kc$ (7.7)

Thus, $K'c = 1 / Kc$ (7.8)

Equilibrium constant for the reverse reaction is the inverse of the equilibrium constant for the reaction in the forward direction.
If we change the stoichiometric coefficients in a chemical equation by multiplying throughout by a factor then we must make sure that the expression for equilibrium constant also reflects that change. For example, if the reaction (7.5) is written as,
$½ H_2(g) + ½ I_2(g) \rightleftharpoons HI(g)$ (7.9)

the equilibrium constant for the above reaction is given by

$K''c = [HI] / [H_2]^{1/2}[I_2]^{1/2} = \{[HI]^2 / [H_2][I_2]\}^{1/2}$

$= x^{1/2} = Kc^{1/2}$ (7.10)

On multiplying the equation (7.5) by n, we get
$nH_2(g) + nI_2(g)$ D $\rightleftharpoons 2nHI(g)$ (7.11)

Therefore, equilibrium constant for the reaction is equal to K_c^n. These findings are summarised in Table 7.4. It should be noted that because the equilibrium constants Kc and K′c have different numerical values, it is important to specify the form of the balanced chemical equation when quoting the value of an equilibrium constant.

Table 7.4 Relations between Equilibrium Constants for a General Reaction and its Multiples.

Chemical equation	Equilibrium constant
$a\,A + b\,B \rightleftharpoons c\,C + d\,D$	K_c
$c\,C + d\,D \rightleftharpoons a\,A + b\,B$	$K_c' = (1/K_c)$
$na\,A + nb\,B \rightleftharpoons nc\,C + nd\,D$	$K_c'' = (K_c^n)$

Problem 7.1

The following concentrations were obtained for the formation of NH_3 from N_2 and H_2 at equilibrium at 500K.

$[N_2] = 1.5 \times 10^{-2}$M. $[H_2] = 3.0 \times 10^{-2}$ M and $[NH_3] = 1.2 \times 10^{-2}$M. Calculate equilibrium constant.

Solution

The equilibrium constant for the reaction,

$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ can be written as,

$$K_c = \frac{[NH_3(g)]^2}{[N_2(g)][H_2(g)]^3}$$

$$= \frac{(1.2 \times 10^{-2})^2}{(1.5 \times 10^{-2})(3.0 \times 10^{-2})^3}$$

$= 0.106 \times 10^4 = 1.06 \times 10^3$

Problem 7.2

At equilibrium, the concentrations of N_2=3.0 × 10^{-3}M, O_2 = 4.2 × 10^{-3}M and

NO= 2.8 × 10^{-3}M in a sealed vessel at 800K. What will be K_c for the reaction

$N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$

Solution

For the reaction equilibrium constant, Kc can be written as,

$$K_c = \frac{[NO]^2}{[N_2][O_2]}$$

$$= \frac{(2.8 \times 10^{-3}\text{M})^2}{(3.0 \times 10^{-3}\text{M})(4.2 \times 10^{-3}\text{M})}$$

= 0.622

7.4 HOMOGENEOUS EQUILIBRIA

In a homogeneous system, all the reactants and products are in the same phase. For example, in the gaseous reaction,

$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$, reactants and products are in the homogeneous phase. Similarly, for the reactions,

$CH_3COOC_2H_5$ (aq) + H_2O (l) $\rightleftharpoons$ CH_3COOH (aq) + C_2H_5OH (aq)

and, Fe^{3+} (aq) + SCN^-(aq) $\rightleftharpoons$ $Fe(SCN)^{2+}$ (aq)

all the reactants and products are in homogeneous solution phase. We shall now consider equilibrium constant for some homogeneous reactions.

7.4.1 Equilibrium Constant in Gaseous Systems

So far we have expressed equilibrium constant of the reactions in terms of molar concentration of the reactants and products, and used symbol, Kc for it. For reactions involving gases, however, it is usually more convenient to express the equilibrium constant in terms of partial pressure.

The ideal gas equation is written as,

pV = nRT

$\Rightarrow \quad p = \frac{n}{V}RT$

Here, p is the pressure in Pa, n is the number of moles of the gas, V is the volume in m^3 and T is the temperature in Kelvin

Therefore,

n/V is concentration expressed in mol/m^3

If concentration c, is in mol/L or mol/dm^3, and p is in bar then

p = cRT,

We can also write p = [gas]RT.

Here, R= 0.0831 bar litre/mol K

At constant temperature, the pressure of the gas is proportional to its concentration i.e.,

$p \propto [gas]$

For reaction in equilibrium

$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$

We can write either

$$K_c = \frac{[HI(g)]^2}{[H_2(g)][I_2(g)]}$$

$$\text{or } K_c = \frac{(p_{HI})^2}{(p_{H_2})(p_{I_2})} \qquad (7.12)$$

Further, since $p_{HI} = [HI(g)]RT$

$$p_{I_2} = [I_2(g)]RT$$

$$p_{H_2} = [H_2(g)]RT$$

Therefore,

$$K_p = \frac{(p_{HI})^2}{(p_{H_2})(p_{I_2})} = \frac{[HI(g)]^2[RT]^2}{[H_2(g)]RT.[I_2(g)]RT}$$

$$= \frac{[HI(g)]^2}{[H_2(g)][I_2(g)]} = K_c \qquad (7.13)$$

In this example, Kp = Kc i.e., both equilibrium constants are equal. However, this is not always the case. For example in reaction

$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

$$K_p = \frac{(p_{NH_3})^2}{(p_{N_2})(p_{H_2})^3}$$

$$= \frac{[NH_3(g)]^2[RT]^2}{[N_2(g)]RT.[H_2(g)]^3(RT)^3}$$

$$= \frac{[NH_3(g)]^2 [RT]^{-2}}{[N_2(g)][H_2(g)]^3} = K_c (RT)^{-2}$$

or $K_p = K_c (RT)^{-2}$ (7.14)

Similarly, for a general reaction

$a\,A + b\,B \rightleftharpoons c\,C + d\,D$

$$K_p = \frac{(p_C^c)(p_D^d)}{(p_A^a)(p_B^b)} = \frac{[C]^c [D]^d (RT)^{(c+d)}}{[A]^a [B]^b (RT)^{(a+b)}}$$

$$= \frac{[C]^c [D]^d}{[A]^a [B]^b} (RT)^{(c+d)-(a+b)}$$

$$= \frac{[C]^c [D]^d}{[A]^a [B]^b} (RT)^{\Delta n} = K_c (RT)^{\Delta n} \quad (7.15)$$

where Δn = (number of moles of gaseous products) – (number of moles of gaseous reactants) in the balanced chemical equation.

It is necessary that while calculating the value of Kp, pressure should be expressed in bar because standard state for pressure is 1 bar. We know from Unit 1 that :

1pascal, Pa=1Nm^{-2}, and 1bar = 10^5 Pa

Kp values for a few selected reactions at different temperatures are given in Table 7.5

Table 7.5 Equilibrium Constants, Kp for a Few Selected Reactions

Reaction	Temperature/K	K_p
$N_2(g) + 3H_2(g) \leftrightharpoons 2NH_3$	298	6.8×10^5
	400	41
	500	3.6×10^{-2}
$2SO_2(g) + O_2(g) \leftrightharpoons 2SO_3(g)$	298	4.0×10^{24}
	500	2.5×10^{10}
	700	3.0×10^4
$N_2O_4(g) \leftrightharpoons 2NO_2(g)$	298	0.98
	400	47.9
	500	1700

Problem 7.3

PCl_5, PCl_3 and Cl_2 are at equilibrium at 500 K and having concentration 1.59M PCl_3, 1.59M Cl_2 and 1.41 M PCl_5. Calculate Kc for the reaction,

$PCl_5 \rightleftharpoons PCl_3 + Cl_2$

Solution

The equilibrium constant Kc for the above reaction can be written as,

$$K_c = \frac{[PCl_3][Cl_2]}{[PCl_5]} = \frac{(1.59)^2}{(1.41)} = 1.79$$

Problem 7.4

The value of Kc = 4.24 at 800K for the reaction,

$CO\ (g) + H_2O\ (g) \rightleftharpoons CO_2\ (g) + H_2\ (g)$

Calculate equilibrium concentrations of CO_2, H_2, CO and H_2O at 800 K, if only CO and H_2O are present initially at concentrations of 0.10M each.

Solution

For the reaction,

$CO\ (g) + H_2O\ (g) \rightleftharpoons CO_2\ (g) + H_2\ (g)$

Initial concentration:

0.1M 0.1M 0 0

Let x mole per litre of each of the product be formed.

At equilibrium:

(0.1-x) M (0.1-x) M x M x M

where x is the amount of CO_2 and H_2 at equilibrium.

Hence, equilibrium constant can be written as,

$Kc = x^2/(0.1-x)^2 = 4.24$

$x^2 = 4.24(0.01 + x^2-0.2x)$

$x^2 = 0.0424 + 4.24x^2-0.848x$

$3.24x^2 – 0.848x + 0.0424 = 0$

$a = 3.24, b = – 0.848, c = 0.0424$

(for quadratic equation $ax^2 + bx + c = 0$,

$$x = \frac{\left(-b \pm \sqrt{b^2 - 4ac}\right)}{2a}$$

$x = 0.848 \pm \sqrt{(0.848)^2 – 4(3.24)(0.0424)}/(3.24 \times 2)$

$x = (0.848 \pm 0.4118)/ 6.48$

$x_1 = (0.848 – 0.4118)/6.48 = 0.067$

$x_2 = (0.848 + 0.4118)/6.48 = 0.194$

the value 0.194 should be neglected because it will give concentration of the reactant which is more than initial concentration.

Hence the equilibrium concentrations are,

$[CO_2] = [H_2-] = x = 0.067$ M

$[CO] = [H_2O] = 0.1 – 0.067 = 0.033$ M

Problem 7.5

For the equilibrium,

$2NOCl(g) \rightleftharpoons 2NO(g) + Cl_2(g)$

the value of the equilibrium constant, Kc is 3.75×10^{-6} at 1069 K. Calculate the Kp for the reaction at this temperature?

Solution

We know that,

$Kp = Kc(RT)\Delta n$

For the above reaction,

$\Delta n = (2+1) - 2 = 1$

$Kp = 3.75 \times 10^{-6} (0.0831 \times 1069)$

$Kp = 0.033$

7.5 HETEROGENEOUS EQUILIBRIA

Equilibrium in a system having more than one phase is called heterogeneous equilibrium. The equilibrium between water vapour and liquid water in a closed container is an example of heterogeneous equilibrium.

$H_2O(l) \rightleftharpoons H_2O(g)$

In this example, there is a gas phase and a liquid phase. In the same way, equilibrium between a solid and its saturated solution,

$Ca(OH)_2\ (s) + (aq) \rightleftharpoons Ca^{2+}\ (aq) + 2OH^-(aq)$

is a heterogeneous equilibrium.

Heterogeneous equilibria often involve pure solids or liquids. We can simplify equilibrium expressions for the heterogeneous equilibria involving a pure liquid or a pure solid, as the molar concentration of a pure solid or liquid is constant (i.e., independent of the amount present). In other words if a substance 'X' is involved, then [X(s)] and [X(l)] are constant, whatever the amount of 'X' is taken. Contrary to this, [X(g)] and [X(aq)] will vary as the amount of X in a given volume varies. Let us take thermal dissociation of calcium carbonate which is an interesting and

important example of heterogeneous chemical equilibrium.

$CaCO_3(s) \underset{}{\overset{\Delta}{\rightleftharpoons}} CaO(s) + CO_2(g)$ (7.16)

On the basis of the stoichiometric equation, we can write,

$$K_c = \frac{[CaO(s)][CO_2(g)]}{[CaCO_3(s)]}$$

Since $[CaCO_3(s)]$ and $[CaO(s)]$ are both constant, therefore modified equilibrium constant for the thermal decomposition of calcium carbonate will be

$$K'_c = [CO_2(g)] \qquad (7.17)$$

$$\text{or } K_p = p_{CO_2} \qquad (7.18)$$

This shows that at a particular temperature, there is a constant concentration or pressure of CO_2 in equilibrium with CaO(s) and $CaCO_3$(s). Experimentally it has been found that at 1100 K, the pressure of CO_2 in equilibrium with $CaCO_3$(s) and CaO(s), is

2.0×10^5 Pa. Therefore, equilibrium constant at 1100K for the above reaction is:

Units of Equilibrium Constant

The value of equilibrium constant K_C can be calculated by substituting the concentration terms in mol/L and for Kp partial pressure is substituted in Pa, kPa, bar or atm. This results in units of equilibrium constant based on molarity or pressure, unless the exponents of both the numerator and denominator are same.

For the reactions,

$H_2(g) + I_2(g) \rightleftharpoons 2HI$, K_C and Kp have no unit.

$N_2O_4(g) \rightleftharpoons 2NO_2(g)$, K_C has unit mol/L and Kp has unit bar

Equilibrium constants can also be expressed as dimensionless quantities if the standard state of reactants and products are specified. For a pure gas, the standard state is 1bar.

Therefore a pressure of 4 bar in standard state can be expressed as 4 bar/1 bar = 4, which is a dimensionless number. Standard state (c_0) for a solute is 1 molar solution and all concentrations can be measured with respect to it. The numerical value of equilibrium constant depends on the standard state chosen. Thus, in this system both Kp and K_C are dimensionless quantities but have different numerical values due to different standard states.

Kp = PCO2 = 2×10^5 Pa/10^5 Pa = 2.00

Similarly, in the equilibrium between nickel, carbon monoxide and nickel carbonyl (used in the purification of nickel),

$Ni\ (s) + 4\ CO\ (g) \rightleftharpoons Ni(CO)_4\ (g)$,

the equilibrium constant is written as

$$K_c = \frac{[Ni(CO)_4]}{[CO]^4}$$

It must be remembered that for the existence of heterogeneous equilibrium pure solids or liquids must also be present (however small the amount may be) at equilibrium, but their concentrations or partial pressures do not appear in the expression of the equilibrium constant. In the reaction,

$Ag_2O(s) + 2HNO_3(aq) \rightleftharpoons 2AgNO_3(aq) + H_2O(l)$

$$K_c = \frac{[AgNO_3]^2}{[HNO_3]^2}$$

Problem 7.6

The value of Kp for the reaction,

$CO_2\ (g) + C\ (s) \rightleftharpoons 2CO\ (g)$

is 3.0 at 1000 K. If initially PCO2 = 0.48 bar and PCO = 0 bar and pure graphite is present,

calculate the equilibrium partial pressures of CO and CO_2.

Solution

For the reaction,

let 'x' be the decrease in pressure of CO_2, then

$CO_2(g) + C(s) \rightleftharpoons 2CO(g)$

Initial

pressure: 0.48 bar 0

At equilibrium:

(0.48 – x)bar 2x bar

$$K_p = \frac{p_{CO}^2}{p_{CO_2}}$$

$Kp = (2x)^2/(0.48 – x) = 3$

$4x^2 = 3(0.48 – x)$

$4x^2 = 1.44 – x$

$4x^2 + 3x – 1.44 = 0$

a = 4, b = 3, c = –1.44

$$x = \frac{\left(-b \pm \sqrt{b^2 - 4ac}\right)}{2a}$$

$= [–3 ± \sqrt{(3)^2 – 4(4)(–1.44)}]/2 × 4$

= (–3 ± 5.66)/8

= (–3 + 5.66)/ 8 (as value of x cannot be negative hence we neglect that value)

x = 2.66/8 = 0.33

The equilibrium partial pressures are,

pCO2= 2x = 2 × 0.33 = 0.66 bar

pCO2= 0.48 – x = 0.48 – 0.33 = 0.15 bar

7.6 APPLICATIONS OF EQUILIBRIUM CONSTANTS

Before considering the applications of equilibrium constants, let us summarise the important features of equilibrium constants as follows:

1. Expression for equilibrium constant is applicable only when concentrations of the reactants and products have attained constant value at equilibrium state.
2. The value of equilibrium constant is independent of initial concentrations of the reactants and products.
3. Equilibrium constant is temperature dependent having one unique value for a particular reaction represented by a balanced equation at a given temperature.
4. The equilibrium constant for the reverse reaction is equal to the inverse of the equilibrium constant for the forward reaction.
5. The equilibrium constant K for a reaction is related to the equilibrium constant of the corresponding reaction, whose equation is obtained by multiplying or dividing the equation for the original reaction by a small integer.

Let us consider applications of equilibrium constant to:

- predict the extent of a reaction on the basis of its magnitude,
- predict the direction of the reaction, and
- calculate equilibrium concentrations.

7.6.1 Predicting the Extent of a Reaction

The numerical value of the equilibrium constant for a reaction indicates the extent of the reaction. But it is important to note that an equilibrium constant does not give any information about the rate at which the equilibrium is reached. The magnitude of K_c or Kp is directly proportional to the concentrations of products (as these appear in the numerator of equilibrium constant expression) and inversely proportional to the concentrations of the reactants (these appear in the denominator). This implies that a high value of K is suggestive of a high concentration of

products and vice-versa.

We can make the following generalisations concerning the composition of equilibrium mixtures:

• If $K_c > 10^3$, products predominate over reactants, i.e., if K_c is very large, the reaction proceeds nearly to completion. Consider the following examples:

(a) The reaction of H_2 with O_2 at 500 K has a very large equilibrium constant,

$K_c = 2.4 \times 10^{47}$.

(b) $H_2(g) + Cl_2(g) \rightleftharpoons 2HCl(g)$ at 300K has

$K_c = 4.0 \times 10^{31}$.

(c) $H_2(g) + Br_2(g) \rightleftharpoons 2HBr\ (g)$ at 300 K,

$Kc = 5.4 \times 10^{18}$

• If $Kc < 10^{-3}$, reactants predominate over products, i.e., if Kc is very small, the reaction proceeds rarely. Consider the following examples:

(a) The decomposition of H_2O into H_2 and O_2 at 500 K has a very small equilibrium constant, $Kc = 4.1 \times 10^{-48}$

(b) $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$,

at 298 K has $Kc = 4.8 \times 10^{-31}$.

• If Kc is in the range of 10^{-3} to 10^3, appreciable concentrations of both reactants and products are present. Consider the following examples:

(a) For reaction of H_2 with I_2 to give HI,

Kc = 57.0 at 700K.

(b) Also, gas phase decomposition of N_2O_4 to NO_2 is another reaction with a value of $Kc = 4.64 \times 10^{-3}$ at 25°C which is neither too small nor too large. Hence, equilibrium mixtures contain appreciable concentrations of

both N_2O_4 and NO_2.

These generarlisations are illustrated in Fig. 7.6

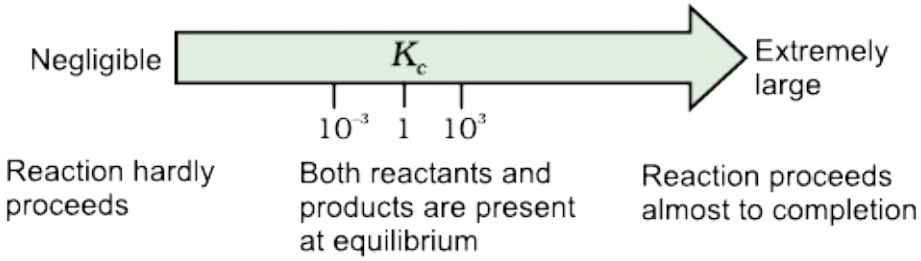


Fig.7.6 Dependence of extent of reaction on Kc

7.6.2 Predicting the Direction of the Reaction

The equilibrium constant helps in predicting the direction in which a given reaction will proceed at any stage. For this purpose, we calculate the **reaction quotient** Q. The reaction quotient, Q (Qc with molar concentrations and QP with partial pressures) is defined in the same way as the equilibrium constant Kc except that the concentrations in Qc are not necessarily equilibrium values.

For a general reaction:

$$a\,A + b\,B \rightleftharpoons c\,C + d\,D \qquad (7.19)$$

$$Qc = [C]^c[D]^d / [A]^a[B]^b \qquad (7.20)$$

Then,

If Qc > Kc, the reaction will proceed in the direction of reactants (reverse reaction).

If Qc < Kc, the reaction will proceed in the direction of the products (forward reaction).

If Qc = Kc, the reaction mixture is already at equilibrium.

Consider the gaseous reaction of H_2 with I_2,

$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$; Kc = 57.0 at 700 K.

Suppose we have molar concentrations $[H_2]_t$=0.10M, $[I_2]_t$ = 0.20 M and $[HI]_t$ = 0.40 M.

(the subscript t on the concentration symbols means that the concentrations were measured at some arbitrary time t, not necessarily at equilibrium).

Thus, the reaction quotient, Qc at this stage of the reaction is given by,

$Qc = [HI]_t^2 / [H_2]_t [I_2]_t = (0.40)^2 / (0.10) \times (0.20) = 8.0$

Now, in this case, Qc (8.0) does not equal Kc (57.0), so the mixture of $H_2(g)$, $I_2(g)$ and HI(g) is not at equilibrium; that is, more $H_2(g)$ and $I_2(g)$ will react to form more HI(g) and their concentrations will decrease till Qc = Kc.

The reaction quotient, Qc is useful in predicting the direction of reaction by comparing the values of Qc and Kc.

Thus, we can make the following generalisations concerning the direction of the reaction (Fig. 7.7) :

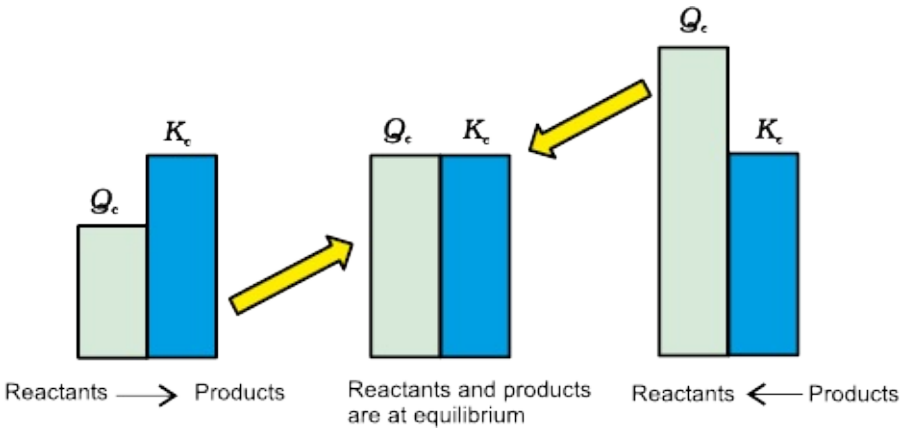


Fig. 7.7 Predicting the direction of the reaction

- If $Q_c < Kc$, net reaction goes from left to right
- If $Q_c > Kc$, net reaction goes from right to left.
- If Qc = Kc, no net reaction occurs.

Problem 7.7

The value of Kc for the reaction

$2A \rightleftharpoons B + C$ is 2×10^{-3}. At a given time, the composition of reaction mixture is

$[A] = [B] = [C] = 3 \times 10^{-4}$ M. In which direction the reaction will proceed?

Solution

For the reaction the reaction quotient Qc is given by,

$Qc = [B][C]/ [A]^2$

as $[A] = [B] = [C] = 3 \times 10^{-4}$M

$Qc = (3 \times 10^{-4})(3 \times 10^{-4}) / (3 \times 10^{-4})^2 = 1$

as Qc > Kc so the reaction will proceed in the reverse direction.

7.6.3 Calculating Equilibrium Concentrations

In case of a problem in which we know the initial concentrations but do not know any of the equilibrium concentrations, the following three steps shall be followed:

Step 1. Write the balanced equation for the reaction.

Step 2. Under the balanced equation, make a table that lists for each substance involved in the reaction:

(a) the initial concentration,

(b) the change in concentration on going to equilibrium, and

(c) the equilibrium concentration.

In constructing the table, define x as the concentration (mol/L) of one of the substances that reacts on going to equilibrium, then use the stoichiometry of the reaction to determine the concentrations of the other substances in terms of x.

Step 3. Substitute the equilibrium concentrations into the equilibrium equation for the reaction and solve for x. If you are to solve a quadratic equation choose the mathematical solution that makes chemical sense.

Step 4. Calculate the equilibrium concentrations from the calculated

value of x.

Step 5. Check your results by substituting them into the equilibrium equation.

Problem 7.8

13.8g of N_2O_4 was placed in a 1L reaction vessel at 400K and allowed to attain equilibrium

$N_2O_4\ (g) \rightleftharpoons 2NO_2\ (g)$

The total pressure at equilbrium was found to be 9.15 bar. Calculate Kc, Kp and partial pressure at equilibrium.

Solution

We know pV = nRT

Total volume (V) = 1 L

Molecular mass of N_2O_4 = 92 g

Number of moles = 13.8g/92 g = 0.15

of the gas (n)

Gas constant (R) = 0.083 bar L $mol^{-1}K^{-1}$

Temperature (T) = 400 K

pV = nRT

p × 1L = 0.15 mol × 0.083 bar L $mol^{-1}K^{-1}$ × 400 K

p = 4.98 bar

N_2O_4 $2NO_2$

Initial pressure: 4.98 bar 0

At equilibrium: (4.98 – x) bar 2x bar Hence,

p_{total} at equilibrium = pN2O4 + pNO2

9.15 = (4.98 – x) + 2x

9.15 = 4.98 + x

x = 9.15 – 4.98 = 4.17 bar

Partial pressures at equilibrium are,

pN2O4 = 4.98 – 4.17 = 0.81bar

pNO2 = 2x = 2 × 4.17 = 8.34 bar

$$K_p = \left(p_{NO_2}\right)^2 / p_{N_2O_4}$$

= $(8.34)^2/0.81 = 85.87$

$Kp = K_c(RT)^{\Delta n}$

$85.87 = Kc(0.083 \times 400)^1$

Kc = 2.586 = 2.6

Problem 7.9

3.00 mol of PCl_5 kept in 1L closed reaction vessel was allowed to attain equilibrium at 380K.

Calculate composition of the mixture at equilibrium. Kc= 1.80

Solution

$PCl_5 \rightleftharpoons PCl_3 + Cl_2$

Initial

concentration: 3.0 0 0

Let x mol per litre of PCl_5 be dissociated,

At equilibrium:

(3-x) x x

$Kc = [PCl_3][Cl_2]/[PCl_5]$

$1.8 = x^2/ (3 – x)$

$x^2 + 1.8x – 5.4 = 0$

$x = [–1.8 \pm \sqrt{(1.8)^2 – 4(–5.4)}]/2$

$x = [–1.8 \pm \sqrt{3.24 + 21.6}]/2$

$x = [–1.8 \pm 4.98]/2$

$x = [–1.8 + 4.98]/2 = 1.59$

$[PCl_5] = 3.0 – x = 3 –1.59 = 1.41$ M

$[PCl_3] = [Cl_2] = x = 1.59$ M

7.7 Relationship between Equilibrium Constant K, Reaction Quotient Q and Gibbs Energy G

The value of Kc for a reaction does not depend on the rate of the reaction. However, as you have studied in Unit 6, it is directly related to the thermodynamics of the reaction and in particular, to the change in Gibbs energy, ΔG. If,

• ΔG is negative, then the reaction is spontaneous and proceeds in the forward direction.

• ΔG is positive, then reaction is considered non-spontaneous. Instead, as reverse reaction would have a negative ΔG, the products of the forward reaction shall be converted to the reactants.

• ΔG is 0, reaction has achieved equilibrium; at this point, there is no longer any free energy left to drive the reaction.

A mathematical expression of this thermodynamic view of equilibrium can be described by the following equation:

$$\Delta G = \Delta G^{\ominus} + RT \ln Q \quad (7.21)$$

where, $G^{\ominus}$ is standard Gibbs energy.

At equilibrium, when $\Delta G = 0$ and $Q = Kc$, the equation (7.21) becomes,

$$\Delta G = \Delta G^{\ominus} + RT \ln K = 0$$

$$\Delta G^{\ominus} = - RT \ln K \quad (7.22)$$

$$\ln K = - \Delta G^{\ominus} / RT$$

Taking antilog of both sides, we get,

$$K = e^{-\Delta G^{\ominus}/RT} \quad (7.23)$$

Hence, using the equation (7.23), the reaction spontaneity can be interpreted in terms of the value of $\Delta G^{\ominus}$.

• If $\Delta G^{\ominus} < 0$, then $-\Delta G^{\ominus}/RT$ is positive, and $e^{-\Delta G^{\ominus}/RT} > 1$, making $K > 1$, which implies a spontaneous reaction or the reaction which proceeds in the forward direction to such an extent that the products are present

predominantly.

• If $\Delta G^{\ominus} > 0$, then $-\Delta G^{\ominus}/RT$ is negative, and $e^{-\Delta G^{\ominus}/RT} < 1$, that is , K < 1, which implies a non-spontaneous reaction or a reaction which proceeds in the forward direction to such a small degree that only a very minute quantity of product is formed.

Problem 7.10

The value of $\Delta G^{\ominus}$ for the phosphorylation of glucose in glycolysis is 13.8 kJ/mol. Find the value of Kc at 298 K.

Solution

$\Delta G^{\ominus} = 13.8$ kJ/mol $= 13.8 \times 10^3$ J/mol

Also, $\Delta G^{\ominus} = -RT \ln Kc$

Hence, $\ln Kc = -13.8 \times 10^3 \text{J/mol} (8.314 \text{ J mol}^{-1}\text{K}^{-1} \times 298 \text{ K})$

$\ln K_C = -5.569$

$K_C = e^{-5.569}$

$K_C = 3.81 \times 10^{-3}$

Problem 7.11

Hydrolysis of sucrose gives,

Sucrose + $H_2O \rightleftharpoons$ Glucose + Fructose

Equilibrium constant Kc for the reaction is 2×10^{13} at 300K. Calculate $\Delta G^{\ominus}$ at 300K.

Solution

$\Delta G^{\ominus} = -RT \ln Kc$

$\Delta G^{\ominus} = -8.314 \text{J mol}^{-1}\text{K}^{-1} \times$

$300\text{K} \times \ln(2 \times 10^{13})$

$\Delta G^{\ominus} = -7.64 \times 10^4 \text{ J mol}^{-1}$

7.8 FACTORS AFFECTING EQUILIBRIA

One of the principal goals of chemical synthesis is to maximise the conversion of the reactants to products while minimizing the expenditure of energy. This implies maximum yield of products at mild temperature and pressure conditions. If it does not happen, then the experimental conditions need to be adjusted. For example, in the Haber process for the synthesis of ammonia from N_2 and H_2, the choice of experimental conditions is of real economic importance. Annual world production of ammonia is about hundred million tones, primarily for use as fertilizers.

Equilibrium constant, Kc is independent of initial concentrations. But if a system at equilibrium is subjected to a change in the concentration of one or more of the reacting substances, then the system is no longer at equilibrium; and net reaction takes place in some direction until the system returns to equilibrium once again. Similarly, a change in temperature or pressure of the system may also alter the equilibrium. In order to decide what course the reaction adopts and make a qualitative prediction about the effect of a change in conditions on equilibrium we use Le Chatelier's principle. It states that a **change in any of the factors that determine the equilibrium conditions of a system will cause the system to change in such a manner so as to reduce or to counteract the effect of the change.** This is applicable to all physical and chemical equilibria.

We shall now be discussing factors which can influence the equilibrium.

7.8.1 Effect of Concentration Change

In general, when equilibrium is disturbed by the addition/removal of any reactant/products, Le Chatelier's principle predicts that:

• The concentration stress of an added reactant/product is relieved by net reaction in the direction that consumes the added substance.

• The concentration stress of a removed reactant/product is relieved by net reaction in the direction that replenishes the removed substance.
or in other words,
“When the concentration of any of the reactants or products in a reaction at equilibrium is changed, the composition of the equilibrium mixture changes so as to minimize the effect of concentration changes”.
Let us take the reaction,
$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$

If H_2 is added to the reaction mixture at equilibrium, then the equilibrium of the reaction is disturbed. In order to restore it, the reaction proceeds in a direction wherein H_2 is consumed, i.e., more of H_2 and I_2 react to form HI and finally the equilibrium shifts in right (forward) direction (Fig.7.8). This is in accordance with the Le Chatelier’s principle which implies that in case of addition of a reactant/product, a new equilibrium will be set up in which the concentration of the reactant/product should be less than what it was after the addition but more than what it was in the original mixture.

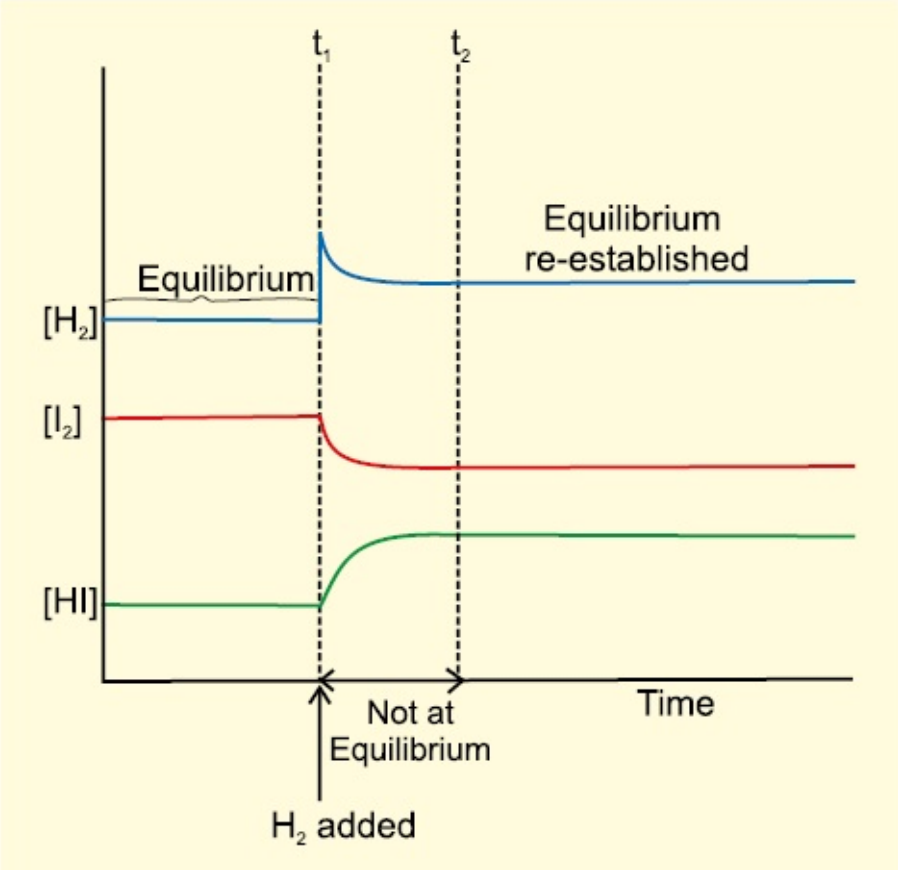


Fig. 7.8 Effect of addition of H2 on change of concentration for the reactants and products in the reaction,

H2(g) + I2 (g) ⇌ 2HI(g)

The same point can be explained in terms of the reaction quotient, Qc,

$Qc = [HI]^2 / [H_2][I_2]$

Addition of hydrogen at equilibrium results in value of Q_c being less than Kc . Thus, in order to attain equilibrium again reaction moves in the forward direction. Similarly, we can say that removal of a product also boosts the forward reaction and increases the concentration of the products and this has great commercial application in cases of reactions, where the product is a gas or a volatile substance. In case of manufacture of ammonia, ammonia is liquified and removed from the reaction mixture so that reaction keeps moving in forward direction. Similarly, in the large scale production of CaO (used as important building

material) from $CaCO_3$, constant removal of CO_2 from the kiln drives the reaction to completion. It should be remembered that continuous removal of a product maintains Qc at a value less than Kc and reaction continues to move in the forward direction.

Effect of Concentration – An experiment

This can be demonstrated by the following reaction:

$$Fe^{3+}(aq) + SCN^{-}(aq) \rightleftharpoons [Fe(SCN)]^{2+}(aq) \qquad (7.24)$$

yellow colourless deep red

$$K_c = \frac{\left[Fe(SCN)^{2+}(aq)\right]}{\left[Fe^{3+}(aq)\right]\left[SCN^{-}(aq)\right]} \qquad (7.25)$$

A reddish colour appears on adding two drops of 0.002 M potassium thiocynate solution to 1 mL of 0.2 M iron(III) nitrate solution due to the formation of $[Fe(SCN)]^{2+}$. The intensity of the red colour becomes constant on attaining equilibrium. This equilibrium can be shifted in either forward or reverse directions depending on our choice of adding a reactant or a product. The equilibrium can be shifted in the opposite direction by adding reagents that remove Fe^{3+} or SCN^{-} ions. For example, oxalic acid ($H_2C_2O_4$), reacts with Fe^{3+} ions to form the stable complex ion $[Fe(C_2O_4)_3]^{3-}$, thus decreasing the concentration of free $Fe^{3+}(aq)$. In accordance with the Le Chatelier's principle, the concentration stress of removed Fe^{3+} is relieved by dissociation of $[Fe(SCN)]^{2+}$ to replenish the Fe^{3+} ions. Because the concentration of $[Fe(SCN)]^{2+}$ decreases, the intensity of red colour decreases.

Addition of aq. $HgCl_2$ also decreases red colour because Hg^{2+} reacts with SCN^{-} ions to form stable complex ion $[Hg(SCN)_4]^{2-}$. Removal of free

SCN^- (aq) shifts the equilibrium in equation (7.24) from right to left to replenish SCN^- ions. Addition of potassium thiocyanate on the other hand increases the colour intensity of the solution as it shift the equilibrium to right.

7.8.2 Effect of Pressure Change

A pressure change obtained by changing the volume can affect the yield of products in case of a gaseous reaction where the total number of moles of gaseous reactants and total number of moles of gaseous products are different. In applying Le Chatelier's principle to a heterogeneous equilibrium the effect of pressure changes on solids and liquids can be ignored because the volume (and concentration) of a solution/liquid is nearly independent of pressure.

Consider the reaction,

$CO(g) + 3H_2(g) \rightleftharpoons CH_4(g) + H_2O(g)$

Here, 4 mol of gaseous reactants ($CO + 3H_2$) become 2 mol of gaseous products ($CH_4 + H_2O$). Suppose equilibrium mixture (for above reaction) kept in a cylinder fitted with a piston at constant temperature is compressed to one half of its original volume. Then, total pressure will be doubled (according to

pV = constant). The partial pressure and therefore, concentration of reactants and products have changed and the mixture is no longer at equilibrium. The direction in which the reaction goes to re-establish equilibrium can be predicted by applying the Le Chatelier's principle. Since pressure has doubled, the equilibrium now shifts in the forward direction, a direction in which the number of moles of the gas or pressure decreases (we know pressure is proportional to moles of the gas). This can also be understood by using reaction quotient, Q_c. Let [CO], $[H_2]$, $[CH_4]$ and $[H_2O]$ be the molar concentrations at equilibrium for

methanation reaction. When volume of the reaction mixture is halved, the partial pressure and the concentration are doubled. We obtain the reaction quotient by replacing each equilibrium concentration by double its value.

$$Q_c = \frac{[CH_4(g)][H_2O(g)]}{[CO(g)][H_2(g)]^3}$$

As $Q_c < Kc$, the reaction proceeds in the forward direction.

In reaction $C(s) + CO_2(g) \quad 2CO(g)$, when pressure is increased, the reaction goes in the reverse direction because the number of moles of gas increases in the forward direction.

7.8.3 Effect of Inert Gas Addition

If the volume is kept constant and an inert gas such as argon is added which does not take part in the reaction, the equilibrium remains undisturbed. It is because the addition of an inert gas at constant volume does not change the partial pressures or the molar concentrations of the substance involved in the reaction. The reaction quotient changes only if the added gas is a reactant or product involved in the reaction.

7.8.4 Effect of Temperature Change

Whenever an equilibrium is disturbed by a change in the concentration, pressure or volume, the composition of the equilibrium mixture changes because the reaction quotient, Q_c no longer equals the equilibrium constant, K_c. However, when a change in temperature occurs, the value of equilibrium constant, Kc is changed.

In general, the temperature dependence of the equilibrium constant depends on the sign of ΔH for the reaction.

- The equilibrium constant for an exothermic reaction (negative ΔH) decreases as the temperature increases.
- The equilibrium constant for an endothermic reaction (positive ΔH)

increases as the temperature increases.

Temperature changes affect the equilibrium constant and rates of reactions.

Production of ammonia according to the reaction,

$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$;

$\Delta H = -92.38 \text{ kJ mol}^{-1}$

is an exothermic process. According to

Le Chatelier's principle, raising the temperature shifts the equilibrium to left and decreases the equilibrium concentration of ammonia. In other words, low temperature is favourable for high yield of ammonia, but practically very low temperatures slow down the reaction and thus a catalyst is used.

Effect of Temperature – An experiment

Effect of temperature on equilibrium can be demonstrated by taking NO_2 gas (brown in colour) which dimerises into N_2O_4 gas (colourless).

$2NO_2(g) \rightleftharpoons N_2O_4(g)$; $\Delta H = -57.2 \text{ kJ mol}^{-1}$

NO_2 gas prepared by addition of Cu turnings to conc. HNO_3 is collected in two 5 mL test tubes (ensuring same intensity of colour of gas in each tube) and stopper sealed with araldite. Three 250 mL beakers 1, 2 and 3 containing freezing mixture, water at room temperature and hot water (363K), respectively, are taken (Fig. 7.9). Both the test tubes are placed in beaker 2 for 8-10 minutes. After this one is placed in beaker 1 and the other in beaker 3. The effect of temperature on direction of reaction is depicted very well in this experiment. At low temperatures in beaker 1, the forward reaction of formation of N_2O_4 is preferred, as reaction is exothermic, and thus, intensity of brown colour due to NO_2 decreases. While in beaker 3, high temperature favours the reverse reaction of

formation of NO_2 and thus, the brown colour intensifies.

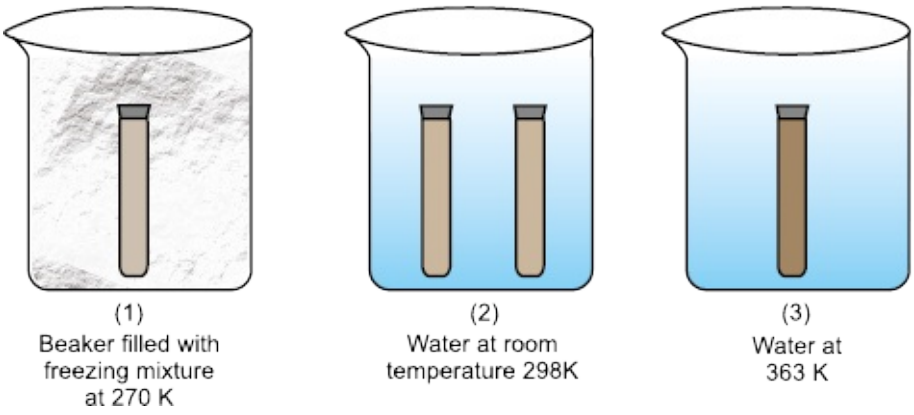


Fig. 7.9 Effect of temperature on equilibrium for the reaction, $2NO_2(g) \rightleftharpoons N_2O_4(g)$

Effect of temperature can also be seen in an endothermic reaction,

$$[Co(H_2O)_6]^{3+}(aq) + 4Cl^-(aq) \rightleftharpoons [CoCl_4]^{2-}(aq) + 6H_2O(l)$$

pink colourless blue

At room temperature, the equilibrium mixture is blue due to $[CoCl_4]^{2-}$. When cooled in a freezing mixture, the colour of the mixture turns pink due to $[Co(H_2O)_6]^{3+}$.

7.8.5 Effect of a Catalyst

A catalyst increases the rate of the chemical reaction by making available a new low energy pathway for the conversion of reactants to products. It increases the rate of forward and reverse reactions that pass through the same transition state and does not affect equilibrium. Catalyst lowers the activation energy for the forward and reverse reactions by exactly the same amount. Catalyst does not affect the equilibrium composition of a reaction mixture. It does not appear in the balanced chemical equation or in the equilibrium constant expression.

Let us consider the formation of NH_3 from dinitrogen and dihydrogen

which is highly exothermic reaction and proceeds with decrease in total number of moles formed as compared to the reactants. Equilibrium constant decreases with increase in temperature. At low temperature rate decreases and it takes long time to reach at equilibrium, whereas high temperatures give satisfactory rates but poor yields.

German chemist, Fritz Haber discovered that a catalyst consisting of iron catalyse the reaction to occur at a satisfactory rate at temperatures, where the equilibrium concentration of NH_3 is reasonably favourable.

Since the number of moles formed in the reaction is less than those of reactants, the yield of NH_3 can be improved by increasing the pressure.

Optimum conditions of temperature and pressure for the synthesis of NH_3 using catalyst are around 500°C and 200 atm.

Similarly, in manufacture of sulphuric acid by contact process,

$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$; $Kc = 1.7 \times 10^{26}$

though the value of K is suggestive of reaction going to completion, but practically the oxidation of SO_2 to SO_3 is very slow. Thus, platinum or divanadium penta-oxide (V_2O_5) is used as catalyst to increase the rate of the reaction.

Note: If a reaction has an exceedingly small K, a catalyst would be of little help.

7.9 IONIC EQUILIBRIUM IN SOLUTION

Under the effect of change of concentration on the direction of equilibrium, you have incidently come across with the following equilibrium which involves ions:

$Fe^{3+}(aq) + SCN^{-}(aq) \rightleftharpoons [Fe(SCN)]^{2+}(aq)$

There are numerous equilibria that involve ions only. In the following sections we will study the equilibria involving ions. It is well known that

the aqueous solution of sugar does not conduct electricity. However, when common salt (sodium chloride) is added to water it conducts electricity. Also, the conductance of electricity increases with an increase in concentration of common salt. Michael Faraday classified the substances into two categories based on their ability to conduct electricity. One category of substances conduct electricity in their aqueous solutions and are called electrolytes while the other do not and are thus, referred to as non-electrolytes. Faraday further classified electrolytes into strong and weak electrolytes. Strong electrolytes on dissolution in water are ionized almost completely, while the weak electrolytes are only partially dissociated. For example, an aqueous solution of sodium chloride is comprised entirely of sodium ions and chloride ions, while that of acetic acid mainly contains unionized acetic acid molecules and only some acetate ions and hydronium ions. This is because there is almost 100% ionization in case of sodium chloride as compared to less than 5% ionization of acetic acid which is a weak electrolyte. It should be noted that in weak electrolytes, equilibrium is established between ions and the unionized molecules. This type of equilibrium involving ions in aqueous solution is called **ionic equilibrium**. Acids, bases and salts come under the category of electrolytes and may act as either strong or weak electrolytes.

7.10 ACIDS, BASES AND SALTS

Acids, bases and salts find widespread occurrence in nature. Hydrochloric acid present in the gastric juice is secreted by the lining of our stomach in a significant amount of 1.2-1.5 L/day and is essential for digestive processes. Acetic acid is known to be the main constituent of vinegar. Lemon and orange juices contain citric and ascorbic acids, and tartaric acid is found in tamarind paste. As most of the acids taste sour, the word “acid” has been derived from a latin word “acidus” meaning

sour. Acids are known to turn blue litmus paper into red and liberate dihydrogen on reacting with some metals. Similarly, bases are known to turn red litmus paper blue, taste bitter and feel soapy. A common example of a base is washing soda used for washing purposes. When acids and bases are mixed in the right proportion they react with each other to give salts. Some commonly known examples of salts are sodium chloride, barium sulphate, sodium nitrate. Sodium chloride (common salt) is an important component of our diet and is formed by reaction between hydrochloric acid and sodium hydroxide. It exists in solid state as a cluster of positively charged sodium ions and negatively charged chloride ions which are held together due to electrostatic interactions between oppositely charged species (Fig.7.10). The electrostatic forces between two charges are inversely proportional to dielectric constant of the medium. Water, a universal solvent, possesses a very high dielectric constant of 80. Thus, when sodium chloride is dissolved in water, the electrostatic interactions are reduced by a factor of 80 and this facilitates the ions to move freely in the solution. Also, they are well-separated due to hydration with water molecules.

Comparing, the ionization of hydrochloric acid with that of acetic acid in water we find that though both of them are polar covalent molecules, former is completely ionized into its constituent ions, while the latter is only partially ionized (< 5%). The extent to which ionization occurs depends upon the strength of the bond and the extent of solvation of ions produced. The terms dissociation and ionization have earlier been used with different meaning. Dissociation refers to the process of separation of ions in water already existing as such in the solid state of the solute, as in sodium chloride. On the other hand, ionization corresponds to a process in which a neutral molecule splits into charged ions in the solution. Here, we shall not distinguish between the two and use the two terms

interchangeably.

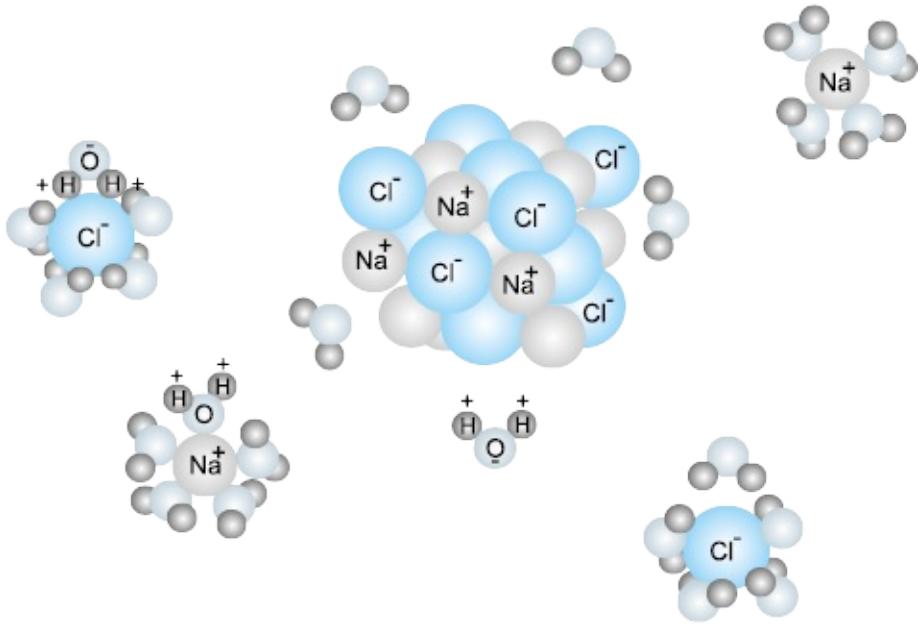


Fig.7.10 Dissolution of sodium chloride in water. Na+ and Cl– ions are stablised by their hydration with polar water molecules.



Michael Faraday

(1791–1867)

Faraday was born near London into a family of very limited means. At the age of 14 he was an apprentice to a kind bookbinder who allowed Faraday to read the books he was binding. Through a fortunate chance he became laboratory assistant to Davy, and during 1813-4, Faraday accompanied him to the Continent. During this trip he gained much from the experience of coming into contact with many of the leading scientists of the time. In 1825, he succeeded Davy as Director of the Royal Institution laboratories, and in 1833 he also became the first Fullerian Professor of Chemistry. Faraday's first important work was on

analytical chemistry. After 1821 much of his work was on electricity and magnetism and different electromagnetic phenomena. His ideas have led to the establishment of modern field theory. He discovered his two laws of electrolysis in 1834. Faraday was a very modest and kind hearted person. He declined all honours and avoided scientific controversies. He preferred to work alone and never had any assistant. He disseminated science in a variety of ways including his Friday evening discourses, which he founded at the Royal Institution. He has been very famous for his Christmas lecture on the 'Chemical History of a Candle'. He published nearly 450 scientific papers.

7.10.1 Arrhenius Concept of Acids and Bases

According to Arrhenius theory, acids are substances that dissociates in water to give hydrogen ions $H^+(aq)$ and bases are substances that produce hydroxyl ions

$OH^-(aq)$. The ionization of an acid HX (aq) can be represented by the following equations:

$HX\ (aq) \rightarrow H^+(aq) + X^-\ (aq)$

or

$HX(aq) + H_2O(l) \rightarrow H_3O^+(aq) + X^-(aq)$

A bare proton, H^+ is very reactive and cannot exist freely in aqueous solutions. Thus, it bonds to the oxygen atom of a solvent water molecule to give trigonal pyramidal **hydronium ion**, H_3O^+ $\{[H\ (H_2O)]^+\}$ (see box).

In this chapter we shall use $H^+(aq)$ and $H_3O^+(aq)$ interchangeably to mean the same i.e., a hydrated proton.

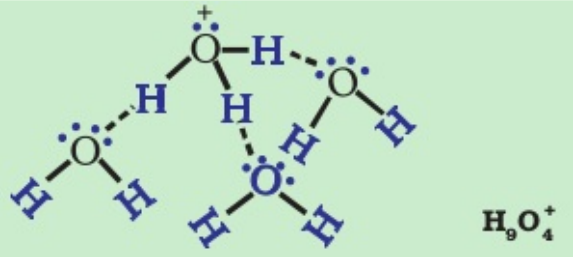
Similarly, a base molecule like MOH ionizes in aqueous solution according to the equation:

$MOH(aq) \rightarrow M^+(aq) + OH^-(aq)$ The hydroxyl ion also exists in the

hydrated form in the aqueous solution. Arrhenius concept of acid and base, however, suffers from the limitation of being applicable only to aqueous solutions and also, does not account for the basicity of substances like, ammonia which do not possess a hydroxyl group.

Hydronium and Hydroxyl Ions

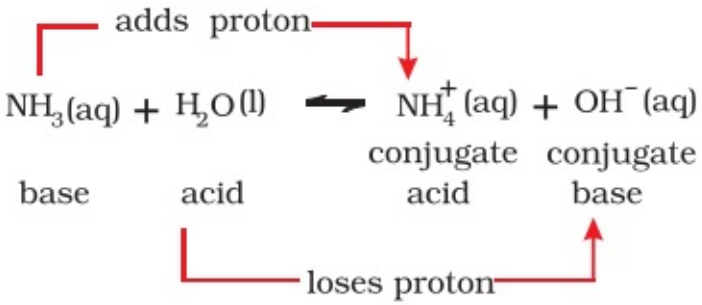
Hydrogen ion by itself is a bare proton with very small size (~10^{-15} m radius) and intense electric field, binds itself with the water molecule at one of the two available lone pairs on it giving H_3O^+. This species has been detected in many compounds (e.g., $H_3O^+Cl^-$) in the solid state. In aqueous solution the hydronium ion is further hydrated to give species like $H_5O_2^+$, $H_7O_3^+$ and $H_9O_4^+$. Similarly the hydroxyl ion is hydrated to give several ionic species like $H_3O_2^-$, $H_5O_3^-$ and $H_7O_4^-$ etc.



7.10.2 The Brönsted-Lowry Acids and Bases

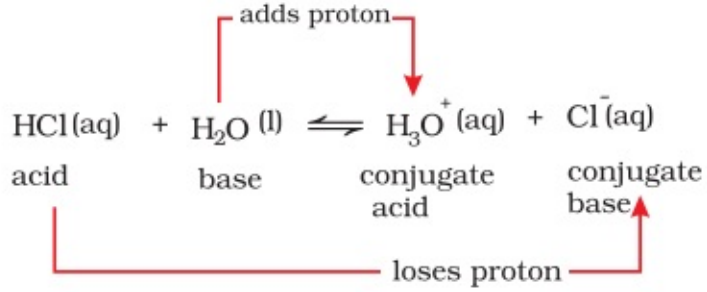
The Danish chemist, Johannes Brönsted and the English chemist, Thomas M. Lowry gave a more general definition of acids and bases. According to Brönsted-Lowry theory, acid is a substance that is capable of donating a hydrogen ion H+ and bases are substances capable of accepting a hydrogen ion, H^+. In short, acids are proton donors and bases are proton acceptors.

Consider the example of dissolution of NH_3 in H_2O represented by the following equation:



The basic solution is formed due to the presence of hydroxyl ions. In this reaction, water molecule acts as proton donor and ammonia molecule acts as proton acceptor and are thus, called Lowry-Brönsted acid and base, respectively. In the reverse reaction, H^+ is transferred from NH_4^+ to OH^-. In this case, NH_4^+ acts as a Bronsted acid while OH^- acted as a Brönsted base. The acid-base pair that differs only by one proton is called a **conjugate acid-base pair**. Therefore, OH^- is called the conjugate base of an acid H_2O and NH_4^+ is called conjugate acid of the base NH_3. If Brönsted acid is a strong acid then **its conjugate base is a weak base and** vice-versa**.** It may be noted that conjugate acid has one extra proton and each conjugate base has one less proton.

Consider the example of ionization of hydrochloric acid in water. HCl(aq) acts as an acid by donating a proton to H_2O molecule which acts as a base.



It can be seen in the above equation, that water acts as a base because

it accepts the proton. The species H_3O^+ is produced when water accepts a proton from HCl. Therefore, Cl^- is a conjugate base of HCl and HCl is the conjugate acid of base Cl^-. Similarly, H_2O is a conjugate base of an acid H_3O^+ and H_3O^+ is a conjugate acid of base H_2O.



Svante Arrhenius

(1859-1927)

was born near Uppsala, Sweden. He presented his thesis, on the conductivities of electrolyte solutions, to the University of Uppsala in 1884. For the next five years he travelled extensively and visited a number of research centers in Europe. In 1895 he was appointed professor of physics at the newly formed University of Stockholm, serving its rector from 1897 to 1902. From 1905 until his death he was Director of physical chemistry at the Nobel Institute in Stockholm. He continued to work for many years on electrolytic solutions. In 1899 he discussed the temperature dependence of reaction rates on the basis of an equation, now usually known as Arrhenius equation.

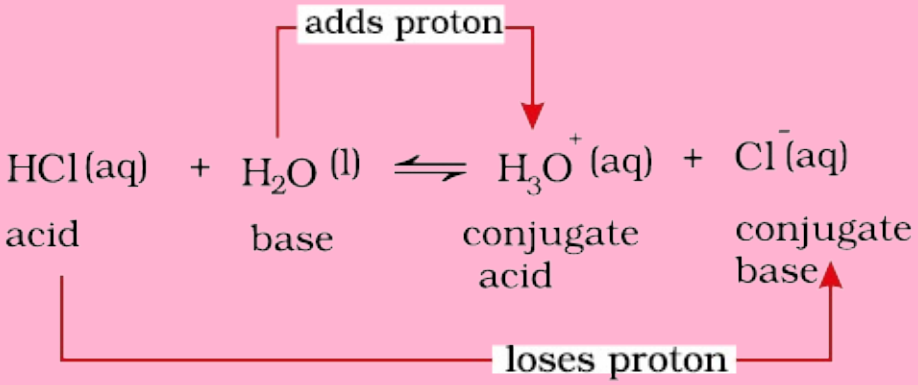
He worked in a variety of fields, and made important contributions to immunochemistry, cosmology, the origin of life, and the causes of ice age. He was the first to discuss the 'green house effect' calling by that name. He received Nobel Prize in Chemistry in 1903 for his theory of electrolytic dissociation and its use in the development of chemistry.

It is interesting to observe the dual role of water as an acid and a base. In case of reaction with HCl water acts as a base while in case of ammonia it acts as an acid by donating a proton.

Problem 7.12

What will be the conjugate bases for the following Brönsted acids: HF, H_2SO_4 and HCO_3^- ?

Solution



The conjugate bases should have one proton less in each case and therefore the corresponding conjugate bases are: F^-, HSO_4^- and CO_3^{2-} respectively.

Problem 7.13

Write the conjugate acids for the following Brönsted bases: NH_2^-, NH_3 and $HCOO^-$.

Solution

The conjugate acid should have one extra proton in each case and therefore the corresponding conjugate acids are: NH_3, NH_4^+ and HCOOH respectively.

Problem 7.14

The species: H_2O, HCO_3^-, HSO_4^- and NH_3 can act both as Bronsted acids and bases. For each case give the corresponding conjugate acid and conjugate base.

Solution

The answer is given in the following Table:

Species	Conjugate acid	Conjugate base
H_2O	H_3O^+	OH^-
HCO_3^-	H_2CO_3	CO_3^{2-}
HSO_4^-	H_2SO_4	SO_4^{2-}
NH_3	NH_4^+	NH_2^-

7.10.3 Lewis Acids and Bases

G.N. Lewis in 1923 defined an acid as a species which accepts electron pair and base which donates an electron pair. As far as bases are concerned, there is not much difference between Brönsted-Lowry and Lewis concepts, as the base provides a lone pair in both the cases. However, in Lewis concept many acids do not have proton. A typical example is reaction of electron deficient species BF_3 with NH_3.

BF_3 does not have a proton but still acts as an acid and reacts with NH_3 by accepting its lone pair of electrons. The reaction can be represented by,

$BF_3 + :NH_3 \rightarrow BF_3:NH_3$

Electron deficient species like $AlCl_3$, Co^{3+}, Mg^{2+}, etc. can act as Lewis acids while species like H_2O, NH_3, OH^- etc. which can donate a pair of electrons, can act as Lewis bases.

Problem 7.15

Classify the following species into Lewis acids and Lewis bases and show how these act as such:

(a) HO^- (b)F^- (c) H^+ (d) BCl_3

Solution

(a) Hydroxyl ion is a Lewis base as it can donate an electron lone pair ($:OH^-$).

(b) Flouride ion acts as a Lewis base as it can donate any one of its four electron lone pairs.

(c) A proton is a Lewis acid as it can accept a lone pair of electrons from bases like hydroxyl ion and fluoride ion.

(d) BCl_3 acts as a Lewis acid as it can accept a lone pair of electrons from species like ammonia or amine molecules.

7.11 IONIZATION OFddddd ACIDS AND BASES

Arrhenius concept of acids and bases becomes useful in case of ionization of acids and bases as mostly ionizations in chemical and biological systems occur in aqueous medium. Strong acids like perchloric acid ($HClO_4$), hydrochloric acid (HCl), hydrobromic acid (HBr), hyrdoiodic acid (HI), nitric acid (HNO_3) and sulphuric acid (H_2SO_4) are termed strong because they are almost completely dissociated into their constituent ions in an aqueous medium, thereby acting as proton (H^+) donors. Similarly, strong bases like lithium hydroxide (LiOH), sodium hydroxide (NaOH), potassium hydroxide (KOH), caesium hydroxide (CsOH) and barium hydroxide $Ba(OH)_2$ are almost completely dissociated into ions in an aqueous medium giving hydroxyl ions, OH^-. According to Arrhenius concept they are strong acids and bases as they are able to completely dissociate and produce H_3O^+ and OH^- ions respectively in the medium. Alternatively, the strength of an acid or base may also be gauged in terms of Brönsted-Lowry concept of acids and bases, wherein a strong acid means a good proton donor and a strong base implies a good proton acceptor. Consider, the acid-base dissociation equilibrium of a weak acid HA,

$$HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq)$$

		conjugate acid	conjugate base
acid	base		

In section 7.10.2 we saw that acid (or base) dissociation equilibrium is dynamic involving a transfer of proton in forward and reverse directions. Now, the question arises that if the equilibrium is dynamic then with passage of time which direction is favoured? What is the driving force behind it? In order to answer these questions we shall deal into the issue of comparing the strengths of the two acids (or bases) involved in the dissociation equilibrium. Consider the two acids HA and H_3O^+ present in the above mentioned acid-dissociation equilibrium. We have to see which amongst them is a stronger proton donor. Whichever exceeds in its tendency of donating a proton over the other shall be termed as the stronger acid and the equilibrium will shift in the direction of weaker acid. Say, if HA is a stronger acid than H_3O^+, then HA will donate protons and not H_3O^+, and the solution will mainly contain A^- and H_3O^+ ions. The equilibrium moves in the direction of formation of weaker acid and weaker base because **the stronger acid donates a proton to the stronger base**.

It follows that as a strong acid dissociates completely in water, the resulting base formed would be very weak i.e., **strong acids have very weak conjugate bases.** Strong acids like perchloric acid ($HClO_4$), hydrochloric acid (HCl), hydrobromic acid (HBr), hydroiodic acid (HI), nitric acid (HNO_3) and sulphuric acid (H_2SO_4) will give conjugate base ions ClO_4^-, Cl, Br^-, I^-, NO_3^- and HSO_4^- , which are much weaker bases than H_2O. Similarly a very strong base would give a very weak conjugate acid. On the other hand, a weak acid say HA is only partially dissociated in aqueous medium and thus, the solution mainly contains undissociated

HA molecules. Typical weak acids are nitrous acid (HNO_2), hydrofluoric acid (HF) and acetic acid (CH_3COOH). It should be noted that the weak acids have very strong conjugate bases. For example, NH_2^-, O^{2-} and H^- are very good proton acceptors and thus, much stronger bases than H_2O.

Certain water soluble organic compounds like phenolphthalein and bromothymol blue behave as weak acids and exhibit different colours in their acid (HIn) and conjugate base (In^-) forms.

$$\underset{\substack{\text{acid}\\ \text{indicator}\\ \text{colour A}}}{HIn(aq)} + H_2O(l) \rightleftharpoons \underset{\substack{\text{conjugate}\\ \text{acid}}}{H_3O^+(aq)} + \underset{\substack{\text{conjugate}\\ \text{base}\\ \text{colourB}}}{In^-(aq)}$$

Such compounds are useful as indicators in acid-base titrations, and finding out H^+ ion concentration.

7.11.1 The Ionization Constant of Water and its Ionic Product

Some substances like water are unique in their ability of acting both as an acid and a base. We have seen this in case of water in section 7.10.2. In presence of an acid, HA it accepts a proton and acts as the base while in the presence of a base, B^- it acts as an acid by donating a proton. In pure water, one H_2O molecule donates proton and acts as an acid and another water molecules accepts a proton and acts as a base at the same time. The following equilibrium exists:

$$\underset{\text{acid}}{H_2O(l)} + \underset{\text{base}}{H_2O(l)} \rightleftharpoons \underset{\substack{\text{conjugate}\\ \text{acid}}}{H_3O^+(aq)} + \underset{\substack{\text{conjugate}\\ \text{base}}}{OH^-(aq)}$$

The dissociation constant is represented by,

$K = [H_3O^+]\,[OH^-] / [H_2O]$ (7.26)

The concentration of water is omitted from the denominator as water is a

pure liquid and its concentration remains constant. $[H_2O]$ is incorporated within the equilibrium constant to give a new constant, K_w, which is called the **ionic product of water**.

$K_w = [H^+][OH^-]$ (7.27)

The concentration of H^+ has been found out experimentally as 1.0×10^{-7} M at 298 K. And, as dissociation of water produces equal number of H^+ and OH^- ions, the concentration of hydroxyl ions, $[OH^-] = [H^+] = 1.0 \times 10^{-7}$ M. Thus, the value of K_w at 298K,

$K_w = [H_3O^+][OH^-] = (1 \times 10^{-7})^2 = 1 \times 10^{-14}\ M^2$ (7.28)

The value of K_w is temperature dependent as it is an equilibrium constant.

The density of pure water is 1000 g / L and its molar mass is 18.0 g /mol. From this the molarity of pure water can be given as,

$[H_2O]$ = (1000 g /L)(1 mol/18.0 g) = 55.55 M.

Therefore, the ratio of dissociated water to that of undissociated water can be given as:

10^{-7} / (55.55) = 1.8×10^{-9} or ~ 2 in 10^{-9} (thus, equilibrium lies mainly towards undissociated water)

We can distinguish acidic, neutral and basic aqueous solutions by the relative values of the H_3O^+ and OH^- concentrations:

Acidic: $[H_3O^+] > [OH^-]$

Neutral: $[H_3O^+] = [OH^-]$

Basic : $[H_3O^+] < [OH^-]$

7.11.2 The pH Scale

Hydronium ion concentration in molarity is more conveniently expressed

on a logarithmic scale known as the **pH scale**. The pH of a solution is defined as the negative logarithm to base 10 of the activity (a_{H^+}) of hydrogen ion. In dilute solutions (< 0.01 M), activity of hydrogen ion (H^+) is equal in magnitude to molarity represented by $[H^+]$. It should be noted that activity has no units and is defined as:

$a_{H^+} = [H^+] / \text{mol } L^{-1}$

From the definition of pH, the following can be written,

$pH = -\log a_{H+} = -\log \{[H^+] / \text{mol } L^{-1}\}$

Thus, an acidic solution of HCl (10^{-2} M) will have a pH = 2. Similarly, a basic solution of NaOH having $[OH^-] = 10^{-4}$ M and $[H_3O^+] =$

10^{-10} M will have a pH = 10. At 25 °C, pure water has a concentration of hydrogen ions,

$[H^+] = 10^{-7}$ M. Hence, the pH of pure water is given as:

$pH = -\log(10^{-7}) = 7$

Acidic solutions possess a concentration of hydrogen ions, $[H^+] > 10^{-7}$ M, while basic solutions possess a concentration of hydrogen ions, $[H^+] < 10^{-7}$ M. thus, we can summarise that

Acidic solution has pH < 7

Basic solution has pH > 7

Neutral solution has pH = 7

Now again, consider the equation (7.28) at 298 K

$K_w = [H_3O^+] [OH^-] = 10^{-14}$

Taking negative logarithm on both sides of equation, we obtain

$-\log K_w = -\log \{[H_3O^+] [OH^-]\}$

$= -\log [H_3O^+] - \log [OH^-]$

$= -\log 10^{-14}$

$pK_w = pH + pOH = 14$ (7.29)

Note that although K_w may change with temperature the variations in pH with temperature are so small that we often ignore it.

pK_w is a very important quantity for aqueous solutions and controls the relative concentrations of hydrogen and hydroxyl ions as their product is a constant. It should be noted that as the pH scale is logarithmic, a change in pH by just one unit also means change in $[H^+]$ by a factor of 10. Similarly, when the hydrogen ion concentration, $[H^+]$ changes by a factor of 100, the value of pH changes by 2 units. Now you can realise why the change in pH with temperature is often ignored.

Measurement of pH of a solution is very essential as its value should be known when dealing with biological and cosmetic applications. The pH of a solution can be found roughly with the help of pH paper that has different colour in solutions of different pH. Now-a-days pH paper is available with four strips on it. The different strips have different colours (Fig. 7.11) at the same pH. The pH in the range of 1-14 can be determined with an accuracy of ~0.5 using pH paper.



Fig.7.11 pH-paper with four strips that may have different colours at the same pH

For greater accuracy pH meters are used. pH meter is a device that measures the pH-dependent electrical potential of the test solution within

0.001 precision. pH meters of the size of a writing pen are now available in the market. The pH of some very common substances are given in Table 7.5 (page 212).

Problem 7.16

The concentration of hydrogen ion in a sample of soft drink is 3.8×10^{-3}M. what is its pH ?

Solution

$pH = -\log[3.8 \times 10^{-3}]$

$= -\{\log[3.8] + \log[10^{-3}]\}$

$= -\{(0.58) + (-3.0)\} = -\{-2.42\} = 2.42$

Therefore, the pH of the soft drink is 2.42 and it can be inferred that it is acidic.

Problem 7.17

Calculate pH of a 1.0×10^{-8} M solution of HCl.

Solution

$2H_2O\,(l) \rightleftharpoons H_3O^+\,(aq) + OH^-(aq)$

$K_w = [OH^-][H_3O^+]$

$= 10^{-14}$

Let, $x = [OH^-] = [H_3O^+]$ from H_2O. The H_3O^+ concentration is generated (i) from the ionization of HCl dissolved i.e.,

$HCl(aq) + H_2O(l) \rightleftharpoons H_3O^+\,(aq) + Cl^-(aq)$,

and (ii) from ionization of H_2O. In these very dilute solutions, both sources of H_3O^+ must be considered:

$[H_3O^+] = 10^{-8} + x$

$K_w = (10^{-8} + x)(x) = 10^{-14}$

or $x^2 + 10^{-8}\,x - 10^{-14} = 0$

$[OH^-] = x = 9.5 \times 10^{-8}$

So, pOH = 7.02 and pH = 6.98

Table 7.5 The pH of Some Common Substances

Name of the Fluid	pH	Name of the Fluid	pH
Saturated solution of NaOH	~15	Black Coffee	5.0
0.1 M NaOH solution	13	Tomato juice	~4.2
Lime water	10.5	Soft drinks and vinegar	~3.0
Milk of magnesia	10	Lemon juice	~2.2
Egg white, sea water	7.8	Gastric juice	~1.2
Human blood	7.4	1M HCl solution	~0
Milk	6.8	Concentrated HCl	~–1.0
Human Saliva	6.4		

7.11.3 Ionization Constants of Weak Acids

Consider a weak acid HX that is partially ionized in the aqueous solution. The equilibrium can be expressed by:

$HX(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + X^-(aq)$

Initial concentration (M)

c 0 0

Let α be the extent of ionization

Change (M)

$-c\alpha$ $+c\alpha$ $+c\alpha$

Equilibrium concentration (M)

$c-c\alpha$ $c\alpha$ $c\alpha$

Here, c = initial concentration of the undissociated acid, HX at time, t = 0. α = extent up to which HX is ionized into ions. Using these notations, we can derive the equilibrium constant for the above discussed acid-dissociation equilibrium:

$K_a = c^2\alpha^2 / c(1-\alpha) = c\alpha^2 / 1-\alpha$

K_a is called the **dissociation or ionization constant** of acid HX. It can be represented alternatively in terms of molar concentration as follows,

$K_a = [H^+][X^-] / [HX]$ (7.30)

At a given temperature T, Ka **is a measure of the strength of the acid HX i.e., larger the value of** Ka**, the stronger is the acid.** Ka **is a dimensionless quantity with the understanding that the standard state concentration of all species is 1M.**

The values of the ionization constants of some selected weak acids are given in Table 7.6.

Table 7.6 The Ionization Constants of Some Selected Weak Acids (at 298K) Acid Ionization Constant

Acid	Ionization Constant, K_a
Hydrofluoric Acid (HF)	3.5×10^{-4}
Nitrous Acid (HNO_2)	4.5×10^{-4}
Formic Acid (HCOOH)	1.8×10^{-4}
Niacin (C_5H_4NCOOH)	1.5×10^{-5}
Acetic Acid (CH_3COOH)	1.74×10^{-5}
Benzoic Acid (C_6H_5COOH)	6.5×10^{-5}
Hypochlorous Acid (HClO)	3.0×10^{-8}
Hydrocyanic Acid (HCN)	4.9×10^{-10}
Phenol (C_6H_5OH)	1.3×10^{-10}

The pH scale for the hydrogen ion concentration has been so useful that besides pK_w, it has been extended to other species and quantities. Thus, we have:

$pK_a = -\log (K_a)$ (7.31)

Knowing the ionization constant, K_a of an acid and its initial concentration, c, it is possible to calculate the equilibrium concentration of all species and also the degree of ionization of the acid and the pH of the solution.

A general step-wise approach can be adopted to evaluate the pH of the weak electrolyte as follows:

Step 1. The species present before dissociation are identified as Brönsted-Lowry
acids / bases.

Step 2. Balanced equations for all possible reactions i.e., with a species acting both as acid as well as base are written.

Step 3. The reaction with the higher K_a is identified as the primary reaction whilst the other is a subsidiary reaction.

Step 4. Enlist in a tabular form the following values for each of the species in the primary reaction

(a) Initial concentration, c.

(b) Change in concentration on proceeding to equilibrium in terms of α, degree of ionization.

(c) Equilibrium concentration.

Step 5. Substitute equilibrium concentrations into equilibrium constant equation for principal reaction and solve for α.

Step 6. Calculate the concentration of species in principal reaction.

Step 7. Calculate pH = $-\log[H_3O^+]$

The above mentioned methodology has been elucidated in the following examples.

Problem 7.18

The ionization constant of HF is

3.2×10^{-4}. Calculate the degree of dissociation of HF in its 0.02 M solution. Calculate the concentration of all species present (H_3O^+, F^- and HF) in the solution and its pH.

Solution

The following proton transfer reactions are possible:

1) $HF + H_2O \rightleftharpoons H_3O^+ + F^-$

$K_a = 3.2 \times 10^{-4}$

2) $H_2O + H_2O \rightleftharpoons H_3O^+ + OH^-$

$K_w = 1.0 \times 10^{-14}$

As $K_a >> K_w$, [1] is the principle reaction.

$HF + H_2O \rightleftharpoons H_3O^+ + F^-$

Initial

concentration (M)

0.02 0 0

Change (M)

–0.02α +0.02α +0.02α

Equilibrium

concentration (M)

0.02 – 0.02 α 0.02 α 0.02α

Substituting equilibrium concentrations in the equilibrium reaction for principal reaction gives:

$K_a = (0.02\alpha)^2 / (0.02 – 0.02\alpha)$

$= 0.02\ \alpha^2 / (1 – \alpha) = 3.2 \times 10^{-4}$

We obtain the following quadratic equation:

$\alpha^2 + 1.6 \times 10^{-2}\alpha – 1.6 \times 10^{-2} = 0$

The quadratic equation in α can be solved and the two values of the roots are:

α = + 0.12 and – 0.12

The negative root is not acceptable and hence,

α = 0.12

This means that the degree of ionization, α = 0.12, then equilibrium concentrations of other species viz., HF, F^- and H_3O^+ are given by:

$[H_3O^+] = [F^-] = c\alpha = 0.02 \times 0.12$

$= 2.4 \times 10^{-3}$ M

$[HF] = c(1 - \alpha) = 0.02\ (1 - 0.12)$

$= 17.6 \times 10^{-3}$ M

$pH = -\log[H^+] = -\log(2.4 \times 10^{-3}) = 2.62$

Problem 7.19

The pH of 0.1M monobasic acid is 4.50. Calculate the concentration of species H^+, A^- and HA at equilibrium. Also, determine the value of Ka and pKa of the monobasic acid.

Solution

$pH = -\log [H^+]$

Therefore, $[H^+] = 10^{-pH} = 10^{-4.50}$

$= 3.16 \times 10^{-5}$

$[H^+] = [A^-] = 3.16 \times 10^{-5}$

Thus, $K_a = [H^+][A^-] / [HA]$

$[HA]_{eqlbm} = 0.1 - (3.16 \times 10^{-5})$ Ä 0.1

$K_a = (3.16 \times 10^{-5})^2 / 0.1 = 1.0 \times 10^{-8}$

$pK_a = -\log(10^{-8}) = 8$

Alternatively, “Percent dissociation” is another useful method for measure of strength of a weak acid and is given as:

Percent dissociation

$= [HA]_{dissociated}/[HA]_{initial} \times 100\%$ (7.32)

Problem 7.20

Calculate the pH of 0.08M solution of hypochlorous acid, HOCl. The ionization constant of the acid is 2.5×10^{-5}. Determine the percent dissociation of HOCl.

Solution

$HOCl(aq) + H_2O\ (l) \rightleftharpoons H_3O^+(aq) + ClO^-(aq)$

Initial concentration (M)

0.08 0 0

Change to reach

equilibrium concentration

(M)

– x + x +x

equilibrium concentartion (M)

0.08 – x x x

$K_a = \{[H_3O^+][ClO^-] / [HOCl]\}$

$= x^2 / (0.08 – x)$

As x << 0.08, therefore 0.08 – x Ä 0.08

$x^2 / 0.08 = 2.5 \times 10^{-5}$

$x^2 = 2.0 \times 10^{-6}$, thus, $x = 1.41 \times 10^{-3}$ $[H^+] = 1.41 \times 10^{-3}$ M.

Therefore,

Percent dissociation

$= \{[HOCl]_{dissociated} / [HOCl]_{initial}\} \times 100$

$= 1.41 \times 10^{-3} \times 10^2 / 0.08 = 1.76$ %.

$pH = -\log(1.41 \times 10^{-3}) = 2.85$.

7.11.4 Ionization of Weak Bases

The ionization of base MOH can be represented by equation:

$MOH(aq) \rightleftharpoons M^+(aq) + OH^-(aq)$

In a weak base there is partial ionization of MOH into M^+ and OH^-, the case is similar to that of acid-dissociation equilibrium. The equilibrium constant for base ionization is called **base ionization constant** and is represented by K_b. It can be expressed in terms of concentration in molarity of various species in equilibrium by the following equation:

$K_b = [M^+][OH^-] / [MOH]$ (7.33)

Alternatively, if c = initial concentration of base and α = degree of ionization of base i.e. the extent to which the base ionizes. When equilibrium is reached, the equilibrium constant can be written as:

$Kb = (c\alpha)^2 / c(1-\alpha) = c\alpha^2 / (1-\alpha)$

The values of the ionization constants of some selected weak bases, Kb are given in

Table 7.7.

Many organic compounds like amines are weak bases. Amines are derivatives of ammonia in which one or more hydrogen atoms are replaced by another group. For example, methylamine, codeine, quinine and nicotine all behave as very weak bases due to their very small K_b.

Ammonia produces OH^- in aqueous solution:

$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$

The pH scale for the hydrogen ion concentration has been extended to get:

pKb = –log (Kb) (7.34)

Table 7.7 The Values of the Ionization Constant of Some Weak Bases at 298 K

Base	K_b
Dimethylamine, $(CH_3)_2NH$	5.4×10^{-4}
Triethylamine, $(C_2H_5)_3N$	6.45×10^{-5}
Ammonia, NH_3 or NH_4OH	1.77×10^{-5}
Quinine, (A plant product)	1.10×10^{-6}
Pyridine, C_5H_5N	1.77×10^{-9}
Aniline, $C_6H_5NH_2$	4.27×10^{-10}
Urea, $CO(NH_2)_2$	1.3×10^{-14}

Problem 7.21

The pH of 0.004M hydrazine solution is 9.7. Calculate its ionization constant K_b and pK_b.

Solution

$NH_2NH_2 + H_2O \rightleftharpoons NH_2NH_3^+ + OH^-$

From the pH we can calculate the hydrogen ion concentration. Knowing hydrogen ion concentration and the ionic product of water we can calculate the concentration of hydroxyl ions. Thus we have:

$[H^+]$ = antilog (–pH)

= antilog (–9.7) = 1.67×10^{-10}

$[OH^-] = K_w / [H^+] = 1 \times 10^{-14} / 1.67 \times 10^{-10}$

$= 5.98 \times 10^{-5}$

The concentration of the corresponding hydrazinium ion is also the same as that of hydroxyl ion. The concentration of both these ions is very small so the concentration of the undissociated base can be taken equal to 0.004M.

Thus,

$K_b = [NH_2NH_3^+][OH^-] / [NH_2NH_2]$

$= (5.98 \times 10^{-5})^2 / 0.004 = 8.96 \times 10^{-7}$

$pK_b = -\log K_b = -\log(8.96 \times 10^{-7}) = 6.04$.

Problem 7.22

Calculate the pH of the solution in which 0.2M NH_4Cl and 0.1M NH_3 are present. The pK_b of ammonia solution is 4.75.

Solution

$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$

The ionization constant of NH_3,

K_b = antilog ($-pK_b$) i.e.

$K_b = 10^{-4.75} = 1.77 \times 10^{-5}$ M

NH_3	+ H_2O ⇌	NH_4^+	+	OH^-
Initial concentration (M)				
0.10		0.20		0
Change to reach equilibrium (M)				
–x		+x		+x
At equilibrium (M)				
0.10 – x		0.20 + x		x

$K_b = [NH_4^+][OH^-] / [NH_3]$

$= (0.20 + x)(x) / (0.1 - x) = 1.77 \times 10^{-5}$

As K_b is small, we can neglect x in comparison to 0.1M and 0.2M. Thus,

$[OH^-] = x = 0.88 \times 10^{-5}$

Therefore, $[H^+] = 1.12 \times 10^{-9}$

$pH = -\log[H^+] = 8.95$.

7.11.5 Relation between Ka and Kb

As seen earlier in this chapter, K_a and K_b represent the strength of an acid and a base, respectively. In case of a conjugate acid-base pair, they are related in a simple manner so that if one is known, the other can be deduced. Considering the example of NH_4^+ and NH_3

we see,

$NH_4^+(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + NH_3(aq)$

$K_a = [H_3O^+][NH_3] / [NH_4^+] = 5.6 \times 10^{-10}$

$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$

$K_b = [NH_4^+][OH^-] / NH_3 = 1.8 \times 10^{-5}$

Net: $2\ H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$

$K_w = [H_3O^+][\ OH^-\ ] = 1.0 \times 10^{-14}$ M

Where, K_a represents the strength of NH_4^+ as an acid and K_b represents the strength of NH_3 as a base.

It can be seen from the net reaction that the equilibrium constant is equal to the product of equilibrium constants K_a and K_b for the reactions added.

Thus,

$K_a \times K_b = \{[H_3O^+][\ NH_3] / [NH_4^+\ ]\} \times \{[NH_4^+\ ]$

$[\ OH^-] / [NH_3]\}$

$= [H_3O^+][\ OH^-] = K_w$

$= (5.6x10^{-10}) \times (1.8 \times 10^{-5}) = 1.0 \times 10^{-14}$ M

This can be extended to make a generalisation. **The equilibrium constant for a net reaction obtained after adding two (or more) reactions equals the product of the equilibrium constants for individual reactions:**

$K_{NET} = K_1 \times K_2 \times$ …… (3.35)

Similarly, in case of a conjugate acid-base pair,

$K_a \times K_b = K_w$ (7.36)

Knowing one, the other can be obtained. It should be noted that a strong acid will have a weak conjugate base and vice-versa.

Alternatively, the above expression

$K_w = K_a \times K_b$, can also be obtained by considering the base-dissociation equilibrium reaction:

$B(aq) + H_2O(l)\ BH^+(aq) + OH^-(aq)$

$K_b = [BH^+][OH^-] / [B]$

As the concentration of water remains constant it has been omitted from

the denominator and incorporated within the dissociation constant. Then multiplying and dividing the above expression by $[H^+]$, we get:

$K_b = [BH^+][OH^-][H^+] / [B][H^+]$

$=\{[OH^-][H^+]\}\{[BH^+] / [B][H^+]\}$

$= K_w / K_a$

or $K_a \times K_b = K_w$

It may be noted that if we take negative logarithm of both sides of the equation, then pK values of the conjugate acid and base are related to each other by the equation:

$pK_a + pK_b = pK_w = 14$ (at 298K)

Problem 7.23

Determine the degree of ionization and pH of a 0.05M of ammonia solution. The ionization constant of ammonia can be taken from Table 7.7. Also, calculate the ionization constant of the conjugate acid of ammonia.

Solution

The ionization of NH_3 in water is represented by equation:

$NH_3 + H_2O \; NH_4^+ + OH^-$

We use equation (7.33) to calculate hydroxyl ion concentration,

$[OH^-] = c\,\alpha = 0.05\,\alpha$

$K_b = 0.05\,\alpha^2 / (1 - \alpha)$

The value of α is small, therefore the quadratic equation can be simplified by neglecting α in comparison to 1 in the denominator on right hand side of the equation,

Thus,

$K_b = c\,\alpha^2$ or $\alpha = \sqrt{(1.77 \times 10^{-5} / 0.05)}$

$= 0.018.$

$[OH^-] = c\,\alpha = 0.05 \times 0.018 = 9.4 \times 10^{-4}$M.

$[H^+] = K_w / [OH^-] = 10^{-14} / (9.4 \times 10^{-4})$

$= 1.06 \times 10^{-11}$

$pH = -\log(1.06 \times 10^{-11}) = 10.97.$

Now, using the relation for conjugate acid-base pair,

$K_a \times K_b = K_w$

using the value of K_b of NH_3 from

Table 7.7.

We can determine the concentration of conjugate acid NH_4^+

$K_a = K_w / K_b = 10^{-14} / 1.77 \times 10^{-5}$

$= 5.64 \times 10^{-10}$.

7.11.6 Di- and Polybasic Acids and Di- and Polyacidic Bases

Some of the acids like oxalic acid, sulphuric acid and phosphoric acids have more than one ionizable proton per molecule of the acid. Such acids are known as polybasic or polyprotic acids.

The ionization reactions for example for a dibasic acid H_2X are represented by the equations:

$H_2X(aq) \rightleftharpoons H^+(aq) + HX^-(aq)$

$HX^-(aq) \rightleftharpoons H^+(aq) + X^{2-}(aq)$

And the corresponding equilibrium constants are given below:

$Ka1 = \{[H^+][HX^-]\} / [H_2X]$ and

$K_a2 = \{[H^+][X^{2-}]\} / [HX^-]$

Here, $K_a1$and $K_a2$are called the first and second ionization constants respectively of the acid H_2 X. Similarly, for tribasic acids like H_3PO_4 we have three ionization constants. The values of the ionization constants for

some common polyprotic acids are given in Table 7.8.

It can be seen that higher order ionization constants (K_a2, K_a3) are smaller than the lower order ionization constant (K_a1) of a polyprotic acid. The reason for this is that it is more difficult to remove a positively charged proton from a negative ion due to electrostatic forces. This can be seen in the case of removing a proton from the uncharged H_2CO_3 as compared from a negatively charged HCO_3^-. Similarly, it is more difficult to remove a proton from a doubly charged HPO_4^{2-} anion as compared to $H_2PO_4^-$.

Polyprotic acid solutions contain a mixture of acids like H_2A, HA^- and A^{2-} in case of a diprotic acid. H_2A being a strong acid, the primary reaction involves the dissociation of H_2 A, and H_3O^+ in the solution comes mainly from the first dissociation step.

Table 7.8 The Ionization Constants of Some Common Polyprotic Acids (298K)

Acid	K_{a_1}	K_{a_2}	K_{a_3}
Oxalic Acid	5.9×10^{-2}	6.4×10^{-5}	
Ascorbic Acid	7.4×10^{-4}	1.6×10^{-12}	
Sulphurous Acid	1.7×10^{-2}	6.4×10^{-8}	
Sulphuric Acid	Very large	1.2×10^{-2}	
Carbonic Acid	4.3×10^{-7}	5.6×10^{-11}	
Citric Acid	7.4×10^{-4}	1.7×10^{-5}	4.0×10^{-7}
Phosphoric Acid	7.5×10^{-3}	6.2×10^{-8}	4.2×10^{-13}

7.11.7 Factors Affecting Acid Strength

Having discussed quantitatively the strengths of acids and bases, we come to a stage where we can calculate the pH of a given acid solution.

But, the curiosity rises about why should some acids be stronger than others? What factors are responsible for making them stronger? The answer lies in its being a complex phenomenon. But, broadly speaking we can say that the extent of dissociation of an acid depends on the **strength** and **polarity** of the H-A bond.

In general, when strength of H-A bond decreases, that is, the energy required to break the bond decreases, HA becomes a stronger acid. Also, when the H-A bond becomes more polar i.e., the electronegativity difference between the atoms H and A increases and there is marked charge separation, cleavage of the bond becomes easier thereby increasing the acidity.

But it should be noted that while comparing elements in the same group of the periodic table, H-A bond strength is a more important factor in determining acidity than its polar nature. As the size of A increases down the group, H-A bond strength decreases and so the acid strength increases. For example,

Size increases Acid strength increases Similarly, H_2S is stronger acid than H_2O.

$$\xrightarrow[\text{HF} << \text{HCl} << \text{HBr} << \text{HI}]{\text{Size increases}} \xrightarrow[]{\text{Acid strength increases}}$$

But, when we discuss elements in the same row of the periodic table, H-A bond polarity becomes the deciding factor for determining the acid strength. As the electronegativity of A increases, the strength of the acid also increases. For example,

$$\xrightarrow[CH_4 < NH_3 < H_2O < HF]{\text{Electronegativity of A increases}} \xrightarrow[]{\text{Acid strength increases}}$$

7.11.8 Common Ion Effect in the Ionization of Acids and Bases

Consider an example of acetic acid dissociation equilibrium represented as:

$CH_3COOH(aq) \rightleftharpoons H^+(aq) + CH_3COO^-(aq)$

or $HAc(aq) \rightleftharpoons H^+(aq) + Ac^-(aq)$

$K_a = [H^+][Ac^-] / [HAc]$

Addition of acetate ions to an acetic acid solution results in decreasing the concentration of hydrogen ions, $[H^+]$. Also, if H^+ ions are added from an external source then the equilibrium moves in the direction of undissociated acetic acid i.e., in a direction of reducing the concentration of hydrogen ions, $[H^+]$. This phenomenon is an example of **common ion effect**. It can be defined as a shift in equilibrium on adding a substance that provides more of an ionic species already present in the dissociation equilibrium. Thus, we can say that common ion effect is a phenomenon based on the Le Chatelier's principle discussed in section 7.8.

In order to evaluate the pH of the solution resulting on addition of 0.05M acetate ion to 0.05M acetic acid solution, we shall consider the acetic acid dissociation equilibrium once again,

$HAc(aq) \rightleftharpoons H^+(aq) + Ac^-(aq)$

Initial concentration (M)		
0.05	0	0.05
Let x be the extent of ionization of acetic acid.		
Change in concentration (M)		
–x	+x	+x
Equilibrium concentration (M)		
0.05-x	x	0.05+x

Therefore,

$K_a = [H^+][Ac^-]/[H\ Ac] = \{(0.05+x)(x)\}/(0.05-x)$

As K_a is small for a very weak acid, $x<<0.05$.

Hence, $(0.05 + x) \approx (0.05 - x) \approx 0.05$

Thus,

$1.8 \times 10^{-5} = (x)\ (0.05 + x) / (0.05 - x)$

$= x(0.05) / (0.05) = x = [H^+] = 1.8 \times 10^{-5}M$

$pH = -\log(1.8 \times 10^{-5}) = 4.74$

Problem 7.24

Calculate the pH of a 0.10M ammonia solution. Calculate the pH after 50.0 mL of this solution is treated with 25.0 mL of 0.10M HCl. The dissociation constant of ammonia, $K_b = 1.77 \times 10^{-5}$

Solution

$NH_3 + H_2O \rightarrow NH_4^+ + OH^-$

$K_b = [NH_4^+][OH^-] / [NH_3] = 1.77 \times 10^{-5}$

Before neutralization,

$[NH_4^+] = [OH^-] = x$

$[NH_3] = 0.10 - x$ Ä 0.10

$x^2 / 0.10 = 1.77 \times 10^{-5}$

Thus, $x = 1.33 \times 10^{-3} = [OH^-]$

Therefore,$[H^+] = K_w / [OH^-] = 10^{-14}$ /

$(1.33 \times 10^{-3}) = 7.51 \times 10^{-12}$

$pH = -\log(7.5 \times 10^{-12}) = 11.12$

On addition of 25 mL of 0.1M HCl solution (i.e., 2.5 mmol of HCl) to 50 mL of 0.1M ammonia

solution (i.e., 5 mmol of NH_3), 2.5 mmol of ammonia molecules are neutralized. The resulting 75 mL solution contains the remaining unneutralized 2.5 mmol of NH_3 molecules and 2.5 mmol of NH_4^+.

$NH_3 + HCl \rightarrow NH_4^+ + Cl^-$

2.5 2.5 0 0

At equilibrium

0 0 2.5 2.5

The resulting 75 mL of solution contains 2.5 mmol of NH_4^+ ions (i.e., 0.033 M) and 2.5 mmol (i.e., 0.033 M) of uneutralised NH_3 molecules. This NH_3 exists in the following equilibrium:

$NH_4OH \rightleftharpoons NH_4^+ + OH^-$

0.033M – y y y

where, $y = [OH^-] = [NH_4^+]$

The final 75 mL solution after neutralisation already contains

2.5 m mol NH_4^+ ions (i.e. 0.033M), thus total concentration of NH_4^+ ions is given as:

$[NH_4^+] = 0.033 + y$

As y is small, $[NH_4OH]$ Ä 0.033 M and $[NH_4^+]$ Ä 0.033M.

We know,

$K_b = [NH_4^+][OH^-] / [NH_4OH]$

$= y(0.033)/(0.033) = 1.77 \times 10^{-5}$ M

Thus, $y = 1.77 \times 10^{-5} = [OH^-]$

$[H^+] = 10^{-14} / 1.77 \times 10^{-5} = 0.56 \times 10^{-9}$

Hence, pH = 9.24

7.11.9 Hydrolysis of Salts and the pH of their Solutions

Salts formed by the reactions between acids and bases in definite

proportions, undergo ionization in water. The cations/anions formed on ionization of salts either exist as hydrated ions in aqueous solutions or interact with water to reform corresponding acids/bases depending upon the nature of salts. The later process of interaction between water and cations/anions or both of salts is called hydrolysis. The pH of the solution gets affected by this interaction. The cations (e.g., Na^+, K^+, Ca^{2+}, Ba^{2+}, etc.) of strong bases and anions (e.g., $Cl^–$, $Br^–$, $NO_3^–$, $ClO_4^–$ etc.) of strong acids simply get hydrated but do not hydrolyse, and therefore the solutions of salts formed from strong acids and bases are neutral i.e., their pH is 7. However, the other category of salts do undergo hydrolysis.

We now consider the hydrolysis of the salts of the following types :

(i) salts of weak acid and strong base e.g., CH_3COONa.

(ii) salts of strong acid and weak base e.g., NH_4Cl, and

(iii) salts of weak acid and weak base, e.g., CH_3COONH_4.

In the first case, CH_3COONa being a salt of weak acid, CH_3COOH and strong base, NaOH gets completely ionised in aqueous solution.

$$CH_3COONa(aq) \rightarrow CH_3COO^–(aq) + Na^+(aq)$$

Acetate ion thus formed undergoes hydrolysis in water to give acetic acid and $OH^–$ ions

$$CH_3COO^–(aq) + H_2O(l) \rightleftharpoons CH_3COOH(aq) + OH^–(aq)$$

Acetic acid being a weak acid

($K_a = 1.8 \times 10^{–5}$) remains mainly unionised in solution. This results in increase of $OH^–$ ion concentration in solution making it alkaline. The pH of such a solution is more than 7.

Similarly, NH_4Cl formed from weak base, NH_4OH and strong acid, HCl, in water dissociates completely.

$NH_4Cl(aq) \rightarrow NH^+_4(aq) + Cl^- (aq)$

Ammonium ions undergo hydrolysis with water to form NH_4OH and H^+ ions

$NH^+_4 (aq) + H_2O (1) \rightleftharpoons NH_4OH(aq) + H^+(aq)$

Ammonium hydroxide is a weak base

($K_b = 1.77 \times 10^{-5}$) and therefore remains almost unionised in solution. This results in increased of H^+ ion concentration in solution making the solution acidic. Thus, the pH of NH_4Cl solution in water is less than 7.

Consider the hydrolysis of CH_3COONH_4 salt formed from weak acid and weak base. The ions formed undergo hydrolysis as follow:

$CH_3COO^- + NH_4^+ + H_2O \rightleftharpoons CH_3COOH + NH_4OH$

CH_3COOH and NH_4OH, also remain into partially dissociated form:

$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$

$NH_4OH \rightleftharpoons NH_4^+ + OH^-$

$H_2O \rightleftharpoons H^+ + OH^-$

Without going into detailed calculation, it can be said that degree of hydrolysis is independent of concentration of solution, and pH of such solutions is determined by their pK values:

$pH = 7 + ½ (pK_a – pK_b)$ (7.38)

The pH of solution can be greater than 7, if the difference is positive and it will be less than 7, if the difference is negative.

Problem 7.25

The pK_a of acetic acid and pKb of ammonium hydroxide are 4.76 and 4.75 respectively. Calculate the pH of ammonium acetate solution.

Solution

$pH = 7 + ½ [pK_a – pK_b]$

$= 7 + ½ [4.76 – 4.75]$

$= 7 + ½ [0.01] = 7 + 0.005 = 7.005$

7.12 BUFFER SOffLUTIONS

Many body fluids e.g., blood or urine have definite pH and any deviation in their pH indicates malfunctioning of the body. The control of pH is also very important in many chemical and biochemical processes. Many medical and cosmetic formulations require that these be kept and administered at a particular pH. **The solutions which resist change in pH on dilution or with the addition of small amounts of acid or alkali are called Buffer Solutions.** Buffer solutions of known pH can be prepared from the knowledge of pK_a of the acid or pK_b of base and by controlling the ratio of the salt and acid or salt and base. A mixture of acetic acid and sodium acetate acts as buffer solution around pH 4.75 and a mixture of ammonium chloride and ammonium hydroxide acts as a buffer around pH 9.25. You will learn more about buffer solutions in higher classes.

7.12.1 Designing Buffer Solution

Knowledge of pKa, pKb and equilibrium constant help us to prepare the buffer solution of known pH. Let us see how we can do this.

Preparation of Acidic Buffer

To prepare a buffer of acidic pH we use weak acid and its salt formed with strong base. We develop the equation relating the pH, the equilibrium constant, Ka of weak acid and ratio of concentration of weak acid and its conjugate base. For the general case where the weak acid

HA ionises in water,

$$HA + H_2O \rightleftharpoons H_3O^+ + A^-$$

For which we can write the expression

$$K_a = \frac{[H_3O^+]\,[A^-]}{[HA]}$$

Rearranging the expression we have,

$$[H_3O^+] = K_a \frac{[HA]}{[A^-]}$$

Taking logarithm on both the sides and rearranging the terms we get —

$$pK_a = pH - \log \frac{[A^-]}{[HA]}$$

Or

$$pH = pK_a + \log \frac{[A^-]}{[HA]} \qquad (7.39)$$

$$pH = pK_a + \log \frac{[\text{Conjugate base}, A^-]}{[\text{Acid}, HA]} \qquad (7.40)$$

The expression (7.40) is known as Henderson–Hasselbalch equation. The quantity $\frac{[A^-]}{[HA]}$ is the ratio of concentration of conjugate base (anion) of the acid and the acid present in the mixture. Since acid is a weak acid, it ionises to a very little extent and concentration of [HA] is negligibly different from concentration of acid taken to form buffer. Also, most of the conjugate base, [A—], comes from the ionisation of salt of the acid. Therefore, the concentration of conjugate base will be negligibly different from the concentration of salt. Thus, equation (7.40) takes the form:

$$pH = pK_a + \log \frac{[\text{Salt}]}{[\text{Acid}]}$$

In the equation (7.39), if the concentration of [A—] is equal to the concentration of [HA], then pH = pKa because value of log 1 is zero.

Thus if we take molar concentration of acid and salt (conjugate base) same, the pH of the buffer solution will be equal to the pKa of the acid. So for preparing the buffer solution of the required pH we select that acid whose pKa is close to the required pH. For acetic acid pKa value is 4.76, therefore pH of the buffer solution formed by acetic acid and sodium acetate taken in equal molar concentration will be around 4.76.

A similar analysis of a buffer made with a weak base and its conjugate acid leads to the result,

$$pOH = pK_b + \log \frac{[\text{Conjugate acid}, BH^+]}{[\text{Base}, B]}$$

pH of the buffer solution can be calculated by using the equation pH + pOH =14.

We know that pH + pOH = pKw and

pKa + pKb = pKw. On putting these values in equation (7.41) it takes the form as follows:

$$pK_w - pH = pK_w - pK_a + \log \frac{[\text{Conjugate acid}, BH^+]}{[\text{Base}, B]}$$

or

$$pH = pK_a + \log \frac{[\text{Conjugate acid}, BH^+]}{[\text{Base}, B]} \quad (7.42)$$

If molar concentration of base and its conjugate acid (cation) is same then pH of the buffer solution will be same as pKa for the base. pKa value for ammonia is 9.25; therefore a buffer of pH close to 9.25 can be obtained by taking ammonia solution and ammonium chloride solution of same molar concentration. For a buffer solution formed by ammonium chloride and ammonium hydroxide, equation

(7.42) becomes:

$$pH = 9.25 + \log \frac{[\text{Conjugate acid}, BH^+]}{[\text{Base}, B]}$$

pH of the buffer solution is not affected by dilution because ratio under the logarithmic term remains unchanged.

7.13 SOLUBILITY EQUILIBRIA OF SPARINGLY SOLUBLE SALTS

We have already known that the solubility of ionic solids in water varies a great deal. Some of these (like calcium chloride) are so soluble that they are hygroscopic in nature and even absorb water vapour from atmosphere. Others (such as lithium fluoride) have so little solubility that they are commonly termed as insoluble. The solubility depends on a number of factors important amongst which are the lattice enthalpy of the salt and the solvation enthalpy of the ions in a solution. For a salt to dissolve in a solvent the strong forces of attraction between its ions (lattice enthalpy) must be overcome by the ion-solvent interactions. The solvation enthalpy of ions is referred to in terms of solvation which is always negative i.e. energy is released in the process of solvation. The amount of solvation enthalpy depends on the nature of the solvent. In case of a non-polar (covalent) solvent, solvation enthalpy is small and hence, not sufficient to overcome lattice enthalpy of the salt. Consequently, the salt does not dissolve in non-polar solvent. As a general rule , for a salt to be able to dissolve in a particular solvent its solvation enthalpy must be greater than its lattice enthalpy so that the latter may be overcome by former. Each salt has its characteristic solubility which depends on temperature. We classify salts on the basis of their solubility in the following three categories.

Category I	Soluble	Solubility > 0.1M
Category II	Slightly Soluble	0.01M<Solubility< 0.1M
Category III	Sparingly Soluble	Solubility < 0.01M

We shall now consider the equilibrium between the sparingly soluble ionic salt and its saturated aqueous solution.

7.13.1 Solubility Product Constant

Let us now have a solid like barium sulphate in contact with its saturated aqueous solution. The equilibrium between the undisolved solid and the ions in a saturated solution can be represented by the equation:

$$BaSO_4(s) \underset{\text{in water}}{\overset{\text{Saturated Solution}}{\rightleftharpoons}} Ba^{2+}(aq) + SO_4^{2-}(aq),$$

The equilibrium constant is given by the equation:

$$K = \{[Ba^{2+}][SO_4^{2-}]\} / [BaSO_4]$$

For a pure solid substance the concentration remains constant and we can write

$$K_{sp} = K[BaSO_4] = [Ba^{2+}][SO_4^{2-}] \quad (7.43)$$

We call K_{sp} the solubility product constant or simply solubility product. The experimental value of K_{sp} in above equation at 298K is

1.1×10^{-10}. This means that for solid barium sulphate in equilibrium with its saturated solution, the product of the concentrations of barium and sulphate ions is equal to its solubility product constant. The concentrations of the two ions will be equal to the molar solubility of the barium sulphate. If molar solubility is S, then

$$1.1 \times 10^{-10} = (S)(S) = S^2$$

or $S = 1.05 \times 10^{-5}$.

Thus, molar solubility of barium sulphate will be equal to 1.05×10^{-5} mol L^{-1}.

A salt may give on dissociation two or more than two anions and cations carrying different charges. For example, consider a salt like zirconium phosphate of molecular formula $(Zr^{4+})_3(PO_4^{3-})_4$. It dissociates into 3

zirconium cations of charge +4 and 4 phosphate anions of charge –3. If the molar solubility of zirconium phosphate is S, then it can be seen from the stoichiometry of the compound that

$[Zr^{4+}] = 3S$ and $[PO_4^{3-}] = 4S$

and $K_{sp} = (3S)^3 (4S)^4 = 6912 (S)^7$

or $S = \{K_{sp} / (3^3 \times 4^4)\}^{1/7} = (K_{sp} / 6912)^{1/7}$

A solid salt of the general formula $M_x^{p+} X_y^{q-}$ with molar solubility S in equilibrium with its saturated solution may be represented by the equation:

$M_xX_y(s) \rightleftharpoons xM^{p+}(aq) + yX^{q-}(aq)$

(where $x \times p^+ = y \times q^-$)

And its solubility product constant is given by:

$K_{sp} = [M^{p+}]^x[X^{q-}]^y = (xS)^x(yS)^y$ (7.44) $= x^x \cdot y^y \cdot S^{(x+y)}$

$S^{(x+y)} = K_{sp} / x^x \cdot y^y$

$S = (K_{sp} / x^x \cdot y^y)^{1/x+y}$ (7.45)

The term K_{sp} in equation is given by Q_{sp} (section 7.6.2) when the concentration of one or more species is not the concentration under equilibrium. Obviously under equilibrium conditions $K_{sp} = Q_{sp}$ but otherwise it gives the direction of the processes of precipitation or dissolution. The solubility product constants of a number of common salts at 298K are given in Table 7.9.

Problem 7.26

Calculate the solubility of A_2X_3 in pure water, assuming that neither kind of ion reacts with water. The solubility product of A_2X_3, $K_{sp} = 1.1 \times 10^{-23}$.

Solution

$A_2X_3 \rightarrow 2A^{3+} + 3X^{2-}$

$K_{sp} = [A^{3+}]^2 [X^{2-}]^3 = 1.1 \times 10^{-23}$

If S = solubility of A_2X_3, then

$[A^{3+}] = 2S$; $[X^{2-}] = 3S$

therefore, $K_{sp} = (2S)^2(3S)^3 = 108S^5$

$= 1.1 \times 10^{-23}$

thus, $S^5 = 1 \times 10^{-25}$

$S = 1.0 \times 10^{-5}$ mol/L.

Problem 7.27

The values of K_{sp} of two sparingly soluble salts $Ni(OH)_2$ and AgCN are 2.0×10^{-15} and 6×0^{-17} respectively. Which salt is more soluble? Explain.

Solution

$AgCN \rightleftharpoons Ag^+ + CN^-$

$K_{sp} = [Ag^+][CN^-] = 6 \times 10^{-17}$

$Ni(OH)_2 \rightleftharpoons Ni^{2+} + 2OH^-$

$K_{sp} = [Ni^{2+}][OH^-]^2 = 2 \times 10^{-15}$

Let $[Ag^+] = S_1$, then $[CN^-] = S_1$

Let $[Ni^{2+}] = S_2$, then $[OH^-] = 2S_2$

$S_1^2 = 6 \times 10^{-17}$, $S_1 = 7.8 \times 10^{-9}$

$(S_2)(2S_2)^2 = 2 \times 10^{-15}$, $S_2 = 0.58 \times 10^{-4}$

$Ni(OH)_2$ is more soluble than AgCN.

Name of the Salt	Formula	K_{sp}
Silver Bromide	$AgBr$	5.0×10^{-13}
Silver Carbonate	Ag_2CO_3	8.1×10^{-12}
Silver Chromate	Ag_2CrO_4	1.1×10^{-12}
Silver Chloride	$AgCl$	1.8×10^{-10}
Silver Iodide	AgI	8.3×10^{-17}
Silver Sulphate	Ag_2SO_4	1.4×10^{-5}
Aluminium Hydroxide	$Al(OH)_3$	1.3×10^{-33}
Barium Chromate	$BaCrO_4$	1.2×10^{-10}
Barium Fluoride	BaF_2	1.0×10^{-6}
Barium Sulphate	$BaSO_4$	1.1×10^{-10}
Calcium Carbonate	$CaCO_3$	2.8×10^{-9}
Calcium Fluoride	CaF_2	5.3×10^{-9}
Calcium Hydroxide	$Ca(OH)_2$	5.5×10^{-6}
Calcium Oxalate	CaC_2O_4	4.0×10^{-9}
Calcium Sulphate	$CaSO_4$	9.1×10^{-6}
Cadmium Hydroxide	$Cd(OH)_2$	2.5×10^{-14}
Cadmium Sulphide	CdS	8.0×10^{-27}
Chromic Hydroxide	$Cr(OH)_3$	6.3×10^{-31}
Cuprous Bromide	$CuBr$	5.3×10^{-9}
Cupric Carbonate	$CuCO_3$	1.4×10^{-10}
Cuprous Chloride	$CuCl$	1.7×10^{-6}
Cupric Hydroxide	$Cu(OH)_2$	2.2×10^{-20}
Cuprous Iodide	CuI	1.1×10^{-12}
Cupric Sulphide	CuS	6.3×10^{-36}
Ferrous Carbonate	$FeCO_3$	3.2×10^{-11}
Ferrous Hydroxide	$Fe(OH)_2$	8.0×10^{-16}
Ferric Hydroxide	$Fe(OH)_3$	1.0×10^{-38}
Ferrous Sulphide	FeS	6.3×10^{-18}
Mercurous Bromide	Hg_2Br_2	5.6×10^{-23}
Mercurous Chloride	Hg_2Cl_2	1.3×10^{-18}
Mercurous Iodide	Hg_2I_2	4.5×10^{-29}
Mercurous Sulphate	Hg_2SO_4	7.4×10^{-7}
Mercuric Sulphide	HgS	4.0×10^{-53}
Magnesium Carbonate	$MgCO_3$	3.5×10^{-8}
Magnesium Fluoride	MgF_2	6.5×10^{-9}
Magnesium Hydroxide	$Mg(OH)_2$	1.8×10^{-11}
Magnesium Oxalate	MgC_2O_4	7.0×10^{-7}
Manganese Carbonate	$MnCO_3$	1.8×10^{-11}
Manganese Sulphide	MnS	2.5×10^{-13}
Nickel Hydroxide	$Ni(OH)_2$	2.0×10^{-15}
Nickel Sulphide	NiS	4.7×10^{-5}
Lead Bromide	$PbBr_2$	4.0×10^{-5}
Lead Carbonate	$PbCO_3$	7.4×10^{-14}
Lead Chloride	$PbCl_2$	1.6×10^{-5}
Lead Fluoride	PbF_2	7.7×10^{-8}
Lead Hydroxide	$Pb(OH)_2$	1.2×10^{-15}
Lead Iodide	PbI_2	7.1×10^{-9}
Lead Sulphate	$PbSO_4$	1.6×10^{-8}
Lead Sulphide	PbS	8.0×10^{-28}
Stannous Hydroxide	$Sn(OH)_2$	1.4×10^{-28}
Stannous Sulphide	SnS	1.0×10^{-25}
Strontium Carbonate	$SrCO_3$	1.1×10^{-10}
Strontium Fluoride	SrF_2	2.5×10^{-9}
Strontium Sulphate	$SrSO_4$	3.2×10^{-7}
Thallous Bromide	$TlBr$	3.4×10^{-6}
Thallous Chloride	$TlCl$	1.7×10^{-4}
Thallous Iodide	TlI	6.5×10^{-8}
Zinc Carbonate	$ZnCO_3$	1.4×10^{-11}
Zinc Hydroxide	$Zn(OH)_2$	1.0×10^{-15}
Zinc Sulphide	ZnS	1.6×10^{-24}

7.13.2 Common Ion Effect on Solubility of Ionic Salts

It is expected from Le Chatelier's principle that if we increase the concentration of any one of the ions, it should combine with the ion of its opposite charge and some of the salt will be precipitated till once again $K_{sp} = Q_{sp}$. Similarly, if the concentration of one of the ions is decreased, more salt will dissolve to increase the concentration of both the ions till once again $K_{sp} = Q_{sp}$. This is applicable even to soluble salts like sodium chloride except that due to higher concentrations of the ions, we use their activities instead of their molarities in the expression for Q_{sp}. Thus if we take a saturated solution of sodium chloride and pass HCl gas through it, then sodium chloride is precipitated due to increased concentration (activity) of chloride ion available from the dissociation of HCl. Sodium chloride thus obtained is of very high purity and we can get rid of impurities like sodium and magnesium sulphates. The common ion effect is also used for almost complete precipitation of a particular ion as its sparingly soluble salt, with very low value of solubility product for gravimetric estimation. Thus we can precipitate silver ion as silver chloride, ferric ion as its hydroxide (or hydrated ferric oxide) and barium ion as its sulphate for quantitative estimations.

Table 7.9 The Solubility Product Constants, K_{sp} of Some Common Ionic Salts at 298K.

Problem 7.28

Calculate the molar solubility of $Ni(OH)_2$ in 0.10 M NaOH. The ionic product of $Ni(OH)_2$ is 2.0×10^{-15}.

Solution

Let the solubility of $Ni(OH)_2$ be equal to S. Dissolution of S mol/L of $Ni(OH)_2$ provides S mol/L of Ni^{2+} and 2S mol/L of OH^-, but the total concentration of OH^- = (0.10 + 2S) mol/L because the solution already contains 0.10 mol/L of OH^- from NaOH.

$K_{sp} = 2.0 \times 10^{-15} = [Ni^{2+}] [OH^-]^2$

$= (S) (0.10 + 2S)^2$

As K_{sp} is small, $2S << 0.10$,

thus, $(0.10 + 2S) \approx 0.10$

Hence,

$2.0 \times 10^{-15} = S (0.10)^2$

$S = 2.0 \times 10^{-13}$ M = $[Ni^{2+}]$

The solubility of salts of weak acids like phosphates increases at lower pH. This is because at lower pH the concentration of the anion decreases due to its protonation. This in turn increase the solubility of the salt so that $K_{sp} = Q_{sp}$. We have to satisfy two equilibria simultaneously i.e.,

$K_{sp} = [M^+] [X^-]$,

$$HX(aq) \rightleftharpoons H^+(aq) + X^-(aq);$$

$$K_a = \frac{[H^+(aq)][X^-(aq)]}{[HX(aq)]}$$

$[X^-] / [HX] = K_a / [H^+]$

Taking inverse of both side and adding 1 we get

$$\frac{[HX]}{[X^-]} + 1 = \frac{[H^+]}{K_a} + 1$$

$$\frac{[HX] + [H^-]}{[X^-]} = \frac{[H^+] + K_a}{K_a}$$

Now, again taking inverse, we get

$[X^-] / \{[X^-] + [HX]\} = f = K_a / (K_a + [H^+])$ and it can be seen that 'f' decreases as pH decreases. If S is the solubility of the salt at a given pH then

$K_{sp} = [S] [f\ S] = S^2 \{K_a / (K_a + [H^+])\}$ and

$S = \{K_{sp} ([H^+] + K_a) / K_a \}^{1/2}$ (7.46)

Thus solubility S increases with increase in $[H^+]$ or decrease in pH.

SUMMARY

When the number of molecules leaving the liquid to vapour equals the number of molecules returning to the liquid from vapour, equilibrium is said to be attained and is dynamic in nature. Equilibrium can be established for both physical and chemical processes and at this stage rate of forward and reverse reactions are equal. Equilibrium constant, Kc is expressed as the concentration of products divided by reactants, each term raised to the stoichiometric coefficient. For reaction, a A + b B c C +d D

$K_C = [C]^c[D]^d/[A]^a[B]^b$

Equilibrium constant has constant value at a fixed temperature and at this stage all the macroscopic properties such as concentration, pressure, etc. become constant. For a gaseous reaction equilibrium constant is expressed as Kp and is written by replacing concentration terms by partial pressures in Kc expression. The direction of reaction can be predicted by reaction quotient Qc which is equal to Kc at equilibrium. Le Chatelier's principle states that the change in any factor such as temperature, pressure, concentration, etc. will cause the equilibrium to shift in such a direction so as to reduce or counteract the effect of the change. It can be used to study the effect of various factors such as temperature, concentration, pressure, catalyst and inert gases on the direction of equilibrium and to control the yield of products by controlling these factors. Catalyst does not effect the equilibrium composition of a reaction mixture but increases the rate of chemical reaction by making available a new lower energy pathway for conversion of

reactants to products and vice-versa.

All substances that conduct electricity in aqueous solutions are called electrolytes. Acids, bases and salts are electrolytes and the conduction of electricity by their aqueous solutions is due to anions and cations produced by the dissociation or ionization of electrolytes in aqueous solution. The strong electrolytes are completely dissociated. In weak electrolytes there is equilibrium between the ions and the unionized electrolyte molecules. According to Arrhenius, acids give hydrogen ions while bases produce hydroxyl ions in their aqueous solutions. Brönsted-Lowry on the other hand, defined an acid as a proton donor and a base as a proton acceptor. When a Brönsted-Lowry acid reacts with a base, it produces its conjugate base and a conjugate acid corresponding to the base with which it reacts. Thus a conjugate pair of acid-base differs only by one proton. Lewis further generalised the definition of an acid as an electron pair acceptor and a base as an electron pair donor. The expressions for ionization (equilibrium) constants of weak acids (K_a) and weak bases (K_b) are developed using Arrhenius definition. The degree of ionization and its dependence on concentration and common ion are discussed. The pH scale ($pH = -\log[H^+]$) for the hydrogen ion concentration (activity) has been introduced and extended to other quantities ($pOH = -\log[OH^-]$) ; $pK_a = -\log[K_a]$;

$pK_b = -\log[K_b]$; and $pK_w = -\log[K_w]$ etc.). The ionization of water has been considered and we note that the equation: $pH + pOH = pK_w$ is always satisfied. The salts of strong acid and weak base, weak acid and strong base, and weak acid and weak base undergo hydrolysis in aqueous solution.The definition of buffer solutions, and their importance are discussed briefly. The solubility equilibrium of sparingly soluble salts is discussed and the equilibrium constant is introduced as solubility product constant (K_{sp}). Its relationship with solubility of the salt is established. The conditions of precipitation of the salt from their solutions or their dissolution in water are worked out. The role of common ion and the solubility of sparingly soluble salts is also discussed.

EXERCISES

7.1 A liquid is in equilibrium with its vapour in a sealed container at a

fixed temperature. The volume of the container is suddenly increased.

a) What is the initial effect of the change on vapour pressure?

b) How do rates of evaporation and condensation change initially?

c) What happens when equilibrium is restored finally and what will be the final vapour pressure?

7.2 What is K_c for the following equilibrium when the equilibrium concentration of each substance is: $[SO_2]$= 0.60M, $[O_2]$ = 0.82M and $[SO_3]$ = 1.90M ?

$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$

7.3 At a certain temperature and total pressure of 10^5Pa, iodine vapour contains 40% by volume of I atoms

$I_2\ (g) \rightleftharpoons 2I\ (g)$

Calculate Kp for the equilibrium.

7.4 Write the expression for the equilibrium constant, Kc for each of the following reactions:

(i) $2NOCl\ (g) \rightleftharpoons 2NO\ (g) + Cl_2\ (g)$

(ii) $2Cu(NO_3)_2\ (s) \rightleftharpoons 2CuO\ (s) + 4NO_2\ (g) + O_2\ (g)$

(iii) $CH_3COOC_2H_5(aq) + H_2O(l) \rightleftharpoons CH_3COOH\ (aq) + C_2H_5OH\ (aq)$

(iv) $Fe^{3+}\ (aq) + 3OH^-\ (aq) \rightleftharpoons Fe(OH)_3\ (s)$

(v) $I_2\ (s) + 5F_2 \rightleftharpoons 2IF_5$

7.5 Find out the value of Kc for each of the following equilibria from the value of Kp:

(i) $2NOCl\ (g) \rightleftharpoons 2NO\ (g) + Cl_2\ (g)$; Kp= 1.8×10^{-2} at 500 K

(ii) $CaCO_3\ (s) \rightleftharpoons CaO(s) + CO_2(g)$; Kp= 167 at 1073 K

7.6 For the following equilibrium, Kc= 6.3×10^{14} at 1000 K

NO (g) + O3 (g) $\rightleftharpoons$ NO2 (g) + O2 (g)

Both the forward and reverse reactions in the equilibrium are elementary bimolecular reactions. What is Kc, for the reverse reaction?

7.7 Explain why pure liquids and solids can be ignored while writing the equilibrium constant expression?

7.8 Reaction between N_2 and O_{2-} takes place as follows:

$2N_2(g) + O_2(g) \rightleftharpoons 2N_2O(g)$

If a mixture of 0.482 mol N_2 and 0.933 mol of O_2 is placed in a 10 L reaction vessel and allowed to form N_2O at a temperature for which $K_c = 2.0 \times 10^{-37}$, determine the composition of equilibrium mixture.

7.9 Nitric oxide reacts with Br_2 and gives nitrosyl bromide as per reaction given below:

$2NO(g) + Br_2(g) \rightleftharpoons 2NOBr(g)$

When 0.087 mol of NO and 0.0437 mol of Br_2 are mixed in a closed container at constant temperature, 0.0518 mol of NOBr is obtained at equilibrium. Calculate equilibrium amount of NO and Br_2 .

7.10 At 450K, $K_p = 2.0 \times 10^{10}$/bar for the given reaction at equilibrium.

$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$

What is Kc at this temperature ?

7.11 A sample of HI(g) is placed in flask at a pressure of 0.2 atm. At equilibrium the partial pressure of HI(g) is 0.04 atm. What is Kp for the given equilibrium ?

$2HI(g) \rightleftharpoons H_2(g) + I_2(g)$

7.12 A mixture of 1.57 mol of N_2, 1.92 mol of H_2 and 8.13 mol of NH_3 is introduced into a 20 L reaction vessel at 500 K. At this temperature, the equilibrium constant, K_c for the reaction $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ is 1.7×10^2. Is the reaction mixture at equilibrium? If not, what is the

direction of the net reaction?

7.13 The equilibrium constant expression for a gas reaction is,

$$K_c = \frac{[NH_3]^4 [O_2]^5}{[NO]^4 [H_2O]^6}$$

Write the balanced chemical equation corresponding to this expression.

7.14 One mole of H_2O and one mole of CO are taken in 10 L vessel and heated to

725 K. At equilibrium 40% of water (by mass) reacts with CO according to the equation,

$H_2O\ (g) + CO\ (g) \rightleftharpoons H_2\ (g) + CO_2\ (g)$

Calculate the equilibrium constant for the reaction.

7.15 At 700 K, equilibrium constant for the reaction:

$H_2\ (g) + I_2\ (g) \rightleftharpoons 2HI\ (g)$

is 54.8. If 0.5 mol L^{-1} of HI(g) is present at equilibrium at 700 K, what are the concentration of $H_2(g)$ and $I_2(g)$ assuming that we initially started with HI(g) and allowed it to reach equilibrium at 700K?

7.16 What is the equilibrium concentration of each of the substances in the equilibrium when the initial concentration of ICl was 0.78 M ?

$2ICl\ (g) \rightleftharpoons I_2\ (g) + Cl_2\ (g)$; Kc = 0.14

7.17 Kp = 0.04 atm at 899 K for the equilibrium shown below. What is the equilibrium concentration of C_2H_6 when it is placed in a flask at 4.0 atm pressure and allowed to come to equilibrium?

$C_2H_6\ (g) \rightleftharpoons C_2H_4\ (g) + H_2\ (g)$

7.18 Ethyl acetate is formed by the reaction between ethanol and acetic acid and the equilibrium is represented as:

$CH_3COOH\ (l) + C_2H_5OH\ (l) \rightleftharpoons CH_3COOC_2H_5\ (l) + H_2O\ (l)$

(i) Write the concentration ratio (reaction quotient), Q_c, for this reaction

(note: water is not in excess and is not a solvent in this reaction)

(ii) At 293 K, if one starts with 1.00 mol of acetic acid and 0.18 mol of ethanol, there is 0.171 mol of ethyl acetate in the final equilibrium mixture. Calculate the equilibrium constant.

(iii) Starting with 0.5 mol of ethanol and 1.0 mol of acetic acid and maintaining it at 293 K, 0.214 mol of ethyl acetate is found after sometime. Has equilibrium been reached?

7.19 A sample of pure PCl_5 was introduced into an evacuated vessel at 473 K. After equilibrium was attained, concentration of PCl_5 was found to be

0.5×10^{-1} mol L^{-1}. If value of K_c is 8.3×10^{-3}, what are the concentrations of PCl_3 and Cl_2 at equilibrium?

$PCl_5\ (g) \rightleftharpoons PCl_3\ (g) + Cl_2(g)$

7.20 One of the reaction that takes place in producing steel from iron ore is the reduction of iron(II) oxide by carbon monoxide to give iron metal and CO_2.

$FeO\ (s) + CO\ (g) \rightleftharpoons Fe\ (s) + CO_2\ (g)$; Kp = 0.265 atm at 1050K

What are the equilibrium partial pressures of CO and CO_2 at 1050 K if the initial partial pressures are: p_{CO}= 1.4 atm and p_{CO_2} = 0.80 atm?

7.21 Equilibrium constant, Kc for the reaction

$N_2\ (g) + 3H_2\ (g) \rightleftharpoons 2NH_3\ (g)$ at 500 K is 0.061

At a particular time, the analysis shows that composition of the reaction mixture is 3.0 mol L^{-1} N_2, 2.0 mol L^{-1} H_2 and 0.5 mol L^{-1} NH_3. Is the reaction at equilibrium? If not in which direction does the reaction tend to proceed to reach equilibrium?

7.22 Bromine monochloride, BrCl decomposes into bromine and chlorine and reaches the equilibrium:

$2BrCl\ (g) \rightleftharpoons Br_2\ (g) + Cl_2\ (g)$

for which K_c= 32 at 500 K. If initially pure BrCl is present at a concentration of

3.3×10^{-3} mol L^{-1}, what is its molar concentration in the mixture at equilibrium?

7.23 At 1127 K and 1 atm pressure, a gaseous mixture of CO and CO_2 in equilibrium with soild carbon has 90.55% CO by mass

$C\ (s) + CO_2\ (g) \rightleftharpoons 2CO\ (g)$

Calculate K_c for this reaction at the above temperature.

7.24 Calculate a) $\Delta G0$ and b) the equilibrium constant for the formation of NO_2 from NO and O_2 at 298K

$NO\ (g) + ½\ O_2\ (g) \rightleftharpoons NO_2\ (g)$

where

$\Delta_f G0\ (NO_2)$ = 52.0 kJ/mol

$\Delta_f G0\ (NO)$ = 87.0 kJ/mol

$\Delta_f G0\ (O_2)$ = 0 kJ/mol

7.25 Does the number of moles of reaction products increase, decrease or remain same when each of the following equilibria is subjected to a decrease in pressure by increasing the volume?

(a) $PCl_5\ (g) \rightleftharpoons PCl_3\ (g) + Cl_2\ (g)$

(b) $CaO\ (s) + CO_2\ (g)\ CaCO_3\ (s)$

(c) $3Fe\ (s) + 4H_2O\ (g)\ Fe_3O_4\ (s) + 4H_2\ (g)$

7.26 Which of the following reactions will get affected by increasing the pressure? Also, mention whether change will cause the reaction to go into forward or backward direction.

(i) $COCl_2\ (g) \rightleftharpoons CO\ (g) + Cl_2\ (g)$

(ii) $CH_4\ (g) + 2S_2\ (g) \rightleftharpoons CS_2\ (g) + 2H_2S\ (g)$

(iii) $CO_2\ (g) + C\ (s) \rightleftharpoons 2CO\ (g)$

(iv) $2H_2\ (g) + CO\ (g) \rightleftharpoons CH_3OH\ (g)$

(v) $CaCO_3\ (s) \rightleftharpoons CaO\ (s) + CO_2\ (g)$

(vi) $4\ NH_3\ (g) + 5O_2\ (g) \rightleftharpoons 4NO\ (g) + 6H_2O(g)$

7.27 The equilibrium constant for the following reaction is 1.6×10^5 at 1024K

$H_2(g) + Br_2(g) \rightleftharpoons 2HBr(g)$

Find the equilibrium pressure of all gases if 10.0 bar of HBr is introduced into a sealed container at 1024K.

7.28 Dihydrogen gas is obtained from natural gas by partial oxidation with steam as per following endothermic reaction:

$CH_4\ (g) + H_2O\ (g) \rightleftharpoons CO\ (g) + 3H_2\ (g)$

(a) Write as expression for Kp for the above reaction.

(b) How will the values of Kp and composition of equilibrium mixture be affected by

(i) increasing the pressure

(ii) increasing the temperature

(iii) using a catalyst ?

7.29 Describe the effect of :

a) addition of H_2

b) addition of CH_3OH

c) removal of CO

d) removal of CH_3OH

on the equilibrium of the reaction:

$2H_2(g) + CO\ (g) \rightleftharpoons CH_3OH\ (g)$

7.30 At 473 K, equilibrium constant Kc for decomposition of phosphorus

pentachloride, PCl_5 is 8.3×10^{-3}. If decomposition is depicted as,

$PCl_5\ (g) \rightleftharpoons PCl_3\ (g) + Cl_2\ (g)\ \Delta_r H0 = 124.0\ kJ\ mol^{-1}$

a) write an expression for Kc for the reaction.

b) what is the value of Kc for the reverse reaction at the same temperature ?

c) what would be the effect on K_c if (i) more PCl_5 is added (ii) pressure is increased (iii) the temperature is increased ?

7.31 Dihydrogen gas used in Haber's process is produced by reacting methane from natural gas with high temperature steam. The first stage of two stage reaction involves the formation of CO and H_2. In second stage, CO formed in first stage is reacted with more steam in water gas shift reaction,

$CO\ (g) + H_2O\ (g) \rightleftharpoons CO_2\ (g) + H_2\ (g)$

If a reaction vessel at 400°C is charged with an equimolar mixture of CO and steam such that pco = pH2O = 4.0 bar, what will be the partial pressure of H_2 at equilibrium? Kp= 10.1 at 400°C

7.32 Predict which of the following reaction will have appreciable concentration of reactants and products:

a) $Cl_2\ (g) \rightleftharpoons 2Cl\ (g)\ Kc = 5 \times 10^{-39}$

b) $Cl_2\ (g) + 2NO\ (g) \rightleftharpoons 2NOCl\ (g)\ K_c = 3.7 \times 10^{8}$

c) $Cl_2\ (g) + 2NO_2\ (g) \rightleftharpoons 2NO_2Cl\ (g)\ Kc = 1.8$

7.33 The value of Kc for the reaction $3O_2\ (g) \rightleftharpoons 2O_3\ (g)$ is 2.0×10^{-50} at 25°C. If the equilibrium concentration of O_2 in air at 25°C is 1.6×10^{-2}, what is the concentration of O_3?

7.34 The reaction, $CO(g) + 3H_2(g) \rightleftharpoons CH_4(g) + H_2O(g)$

is at equilibrium at 1300 K in a 1L flask. It also contain 0.30 mol of CO, 0.10 mol of H_2 and 0.02 mol of H_2O and an unknown amount of CH_4 in the flask. Determine the concentration of CH_4 in the mixture. The equilibrium constant, Kc for the reaction at the given temperature is 3.90.

7.35 What is meant by the conjugate acid-base pair? Find the conjugate acid/base for the following species:

HNO_2, CN^-, $HClO_4$, F^-, OH^-, CO_3^{2-}, and S^{2-}

7.36 Which of the followings are Lewis acids? H_2O, BF_3, H^+, and NH_4^+

7.37 What will be the conjugate bases for the Brönsted acids: HF, H_2SO_4 and HCO^-_3?

7.38 Write the conjugate acids for the following Brönsted bases: NH_2^-, NH_3 and $HCOO^-$.

7.39 The species: H_2O, HCO_3^-, HSO_4^- and NH_3 can act both as Brönsted acids and bases. For each case give the corresponding conjugate acid and base.

7.40 Classify the following species into Lewis acids and Lewis bases and show how these act as Lewis acid/base: (a) OH^- (b) F^- (c) H^+ (d) BCl_3 .

7.41 The concentration of hydrogen ion in a sample of soft drink is 3.8×10^{-3} M. what is its pH?

7.42 The pH of a sample of vinegar is 3.76. Calculate the concentration of hydrogen ion in it.

7.43 The ionization constant of HF, HCOOH and HCN at 298K are 6.8×10^{-4},

1.8×10^{-4} and 4.8×10^{-9} respectively. Calculate the ionization constants of the corresponding conjugate base.

7.44 The ionization constant of phenol is 1.0×10^{-10}. What is the concentration of phenolate ion in 0.05 M solution of phenol? What will be its degree of ionization if the solution is also 0.01M in sodium phenolate?

7.45 The first ionization constant of H_2S is 9.1×10^{-8}. Calculate the concentration of HS^- ion in its 0.1M solution. How will this concentration be affected if the solution is 0.1M in HCl also ? If the second dissociation constant of H_2S is

1.2×10^{-13}, calculate the concentration of S^{2-} under both conditions.

7.46 The ionization constant of acetic acid is 1.74×10^{-5}. Calculate the degree of dissociation of acetic acid in its 0.05 M solution. Calculate the concentration of acetate ion in the solution and its pH.

7.47 It has been found that the pH of a 0.01M solution of an organic acid is 4.15. Calculate the concentration of the anion, the ionization constant of the acid and its pK_a.

7.48 Assuming complete dissociation, calculate the pH of the following solutions:

(a) 0.003 M HCl (b) 0.005 M NaOH (c) 0.002 M HBr (d) 0.002 M KOH

7.49 Calculate the pH of the following solutions:

a) 2 g of TlOH dissolved in water to give 2 litre of solution.

b) 0.3 g of $Ca(OH)_2$ dissolved in water to give 500 mL of solution.

c) 0.3 g of NaOH dissolved in water to give 200 mL of solution.

d) 1mL of 13.6 M HCl is diluted with water to give 1 litre of solution.

7.50 The degree of ionization of a 0.1M bromoacetic acid solution is 0.132. Calculate the pH of the solution and the pK_a of bromoacetic acid.

7.51 The pH of 0.005M codeine ($C_{18}H_{21}NO_3$) solution is 9.95. Calculate its ionization constant and pK_b.

7.52 What is the pH of 0.001M aniline solution ? The ionization constant

of aniline can be taken from Table 7.7. Calculate the degree of ionization of aniline in the solution. Also calculate the ionization constant of the conjugate acid of aniline.

7.53 Calculate the degree of ionization of 0.05M acetic acid if its pK_a value is 4.74. How is the degree of dissociation affected when its solution also contains

(a) 0.01M (b) 0.1M in HCl ?

7.54 The ionization constant of dimethylamine is 5.4×10^{-4}. Calculate its degree of ionization in its 0.02M solution. What percentage of dimethylamine is ionized if the solution is also 0.1M in NaOH?

7.55 Calculate the hydrogen ion concentration in the following biological fluids whose pH are given below:

(a) Human muscle-fluid, 6.83 (b) Human stomach fluid, 1.2

(c) Human blood, 7.38 (d) Human saliva, 6.4.

7.56 The pH of milk, black coffee, tomato juice, lemon juice and egg white are 6.8, 5.0, 4.2, 2.2 and 7.8 respectively. Calculate corresponding hydrogen ion concentration in each.

7.57 If 0.561 g of KOH is dissolved in water to give 200 mL of solution at 298 K. Calculate the concentrations of potassium, hydrogen and hydroxyl ions. What is its pH?

7.58 The solubility of $Sr(OH)_2$ at 298 K is 19.23 g/L of solution. Calculate the concentrations of strontium and hydroxyl ions and the pH of the solution.

7.59 The ionization constant of propanoic acid is 1.32×10^{-5}. Calculate the degree of ionization of the acid in its 0.05M solution and also its pH. What will be its degree of ionization if the solution is 0.01M in HCl also?

7.60 The pH of 0.1M solution of cyanic acid (HCNO) is 2.34. Calculate the ionization constant of the acid and its degree of ionization in the solution.

7.61 The ionization constant of nitrous acid is 4.5×10^{-4}. Calculate the pH of 0.04 M sodium nitrite solution and also its degree of hydrolysis.

7.62 A 0.02M solution of pyridinium hydrochloride has pH = 3.44. Calculate the ionization constant of pyridine.

7.63 Predict if the solutions of the following salts are neutral, acidic or basic:

NaCl, KBr, NaCN, NH_4NO_3, $NaNO_2$ and KF

7.64 The ionization constant of chloroacetic acid is 1.35×10^{-3}. What will be the pH of 0.1M acid and its 0.1M sodium salt solution?

7.65 Ionic product of water at 310 K is 2.7×10^{-14}. What is the pH of neutral water at this temperature?

7.66 Calculate the pH of the resultant mixtures:

a) 10 mL of 0.2M $Ca(OH)_2$ + 25 mL of 0.1M HCl

b) 10 mL of 0.01M H_2SO_4 + 10 mL of 0.01M $Ca(OH)_2$

c) 10 mL of 0.1M H_2SO_4 + 10 mL of 0.1M KOH

7.67 Determine the solubilities of silver chromate, barium chromate, ferric hydroxide, lead chloride and mercurous iodide at 298K from their solubility product constants given in Table 7.9. Determine also the molarities of individual ions.

7.68 The solubility product constant of Ag_2CrO_4 and AgBr are 1.1×10^{-12} and

5.0×10^{-13} respectively. Calculate the ratio of the molarities of their saturated solutions.

7.69 Equal volumes of 0.002 M solutions of sodium iodate and cupric chlorate are mixed together. Will it lead to precipitation of copper iodate? (For cupric iodate

$K_{sp} = 7.4 \times 10^{-8}$).

7.70 The ionization constant of benzoic acid is 6.46×10^{-5} and K_{sp} for silver benzoate is 2.5×10^{-13}. How many times is silver benzoate more soluble in a buffer of pH 3.19 compared to its solubility in pure water?

7.71 What is the maximum concentration of equimolar solutions of ferrous sulphate and sodium sulphide so that when mixed in equal volumes, there is no precipitation of iron sulphide? (For iron sulphide, $K_{sp} = 6.3 \times 10^{-18}$).

7.72 What is the minimum volume of water required to dissolve 1g of calcium sulphate at 298 K? (For calcium sulphate, K_{sp} is 9.1×10^{-6}).

7.73 The concentration of sulphide ion in 0.1M HCl solution saturated with hydrogen sulphide is 1.0×10^{-19} M. If 10 mL of this is added to 5 mL of 0.04 M solution of the following: $FeSO_4$, $MnCl_2$, $ZnCl_2$ and $CdCl_2$. in which of these solutions precipitation will take place?

SUGGESTED ACTIVITIES FOR STUDENTS REGARDING THIS UNIT

(a) The student may use pH paper in determining the pH of fresh juices of various vegetables and fruits, soft drinks, body fluids and also that of water samples available.

(b) The pH paper may also be used to determine the pH of different salt solutions and from that he/she may determine if these are formed from strong/weak acids and bases.

(c) They may prepare some buffer solutions by mixing the solutions of sodium acetate and acetic acid and determine their pH using pH paper.

(d) They may be provided with different indicators to observe their colours in solutions of varying pH.

(e) They may perform some acid-base titrations using indicators.

(f) They may observe common ion effect on the solubility of sparingly soluble salts.

(g) If pH meter is available in their school, they may measure the pH with

it and compare the results obtained with that of the pH paper.

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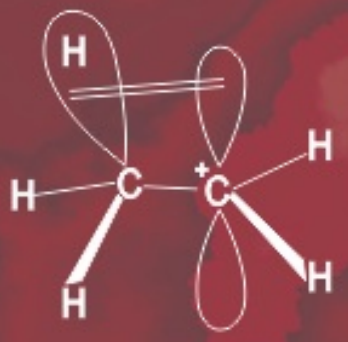
Textbook for Class XI



Unit 8
Redox Reactions

Chemistry

Part II



11083CH08

UNIT 8

Redox Reactions

Objectives

After studying this unit you will be able to

• identify redox reactions as a class of reactions in which oxidation and reduction reactions occur simultaneously;

• define the terms oxidation, reduction, oxidant (oxidising agent) and reductant (reducing agent);

• explain mechanism of redox reactions by electron transfer process;

• use the concept of oxidation number to identify oxidant and reductant in a reaction;

• classify redox reaction into combination (synthesis), decomposition, displacement and disproportionation reactions;

• suggest a comparative order among various reductants and oxidants;

• balance chemical equations using (i) oxidation number (ii) half reaction method;

• learn the concept of redox reactions in terms of electrode processes.

"Where there is oxidation, there is always reduction – Chemistry is essentially a study of redox systems."

Chemistry deals with varieties of matter and change of one kind of matter into the other. Transformation of matter from one kind into another occurs through the various types of reactions. One important category of such reactions is Redox Reactions. A number of phenomena, both physical as well as biological, are concerned with redox reactions. These reactions find extensive use in pharmaceutical, biological, industrial, metallurgical and agricultural areas. The importance of these reactions is apparent from the fact that burning of different types of fuels for obtaining energy for domestic, transport and other commercial purposes, electrochemical processes for extraction of highly reactive metals and non-metals, manufacturing of chemical compounds like caustic soda, operation of dry and wet batteries and corrosion of metals fall within the purview of redox processes. Of late, environmental issues like Hydrogen Economy (use of liquid hydrogen as fuel) and development of 'Ozone Hole' have started figuring under redox phenomenon.

8.1 CLASSICAL IDEA OF REDOX REACTIONS – OXIDATION AND REDUCTION REACTIONS

Originally, the term oxidation was used to describe the addition of oxygen to an element or a compound. Because of the presence of dioxygen in the atmosphere (~20%), many elements combine with it and this is the principal reason why they commonly occur on the earth in the form of their oxides. The following reactions represent oxidation processes according to the limited definition of oxidation:

$$2\ Mg\ (s) + O_2\ (g) \rightarrow 2\ MgO\ (s)\ (8.1)$$

$$S\ (s) + O_2\ (g) \rightarrow SO_2\ (g)\ (8.2)$$

In reactions (8.1) and (8.2), the elements magnesium and sulphur are oxidised on account of addition of oxygen to them. Similarly, methane is oxidised owing to the addition of oxygen to it.

$$CH_4\ (g) + 2O_2\ (g) \rightarrow CO_2\ (g) + 2H_2O\ (l) \qquad (8.3)$$

A careful examination of reaction (8.3) in which hydrogen has been replaced by oxygen prompted chemists to reinterpret oxidation in terms of removal of hydrogen from it and, therefore, the scope of term oxidation was broadened to include the removal of hydrogen from a substance. The following illustration is another reaction where removal of hydrogen can also be cited as an oxidation reaction.

$$2\ H_2S(g) + O_2\ (g) \rightarrow 2\ S\ (s) + 2\ H_2O\ (l) \qquad (8.4)$$

As knowledge of chemists grew, it was natural to extend the term oxidation for reactions similar to (8.1 to 8.4), which do not involve oxygen but other electronegative elements. The oxidation of magnesium with fluorine, chlorine and sulphur etc. occurs according to the following reactions :

$$Mg\ (s) + F_2\ (g) \rightarrow MgF_2\ (s) \qquad (8.5)$$

$$Mg\ (s) + Cl_2\ (g) \rightarrow MgCl_2\ (s) \qquad (8.6)$$

$$Mg\ (s) + S\ (s) \rightarrow MgS\ (s) \qquad (8.7)$$

Incorporating the reactions (8.5 to 8.7) within the fold of oxidation reactions encouraged chemists to consider not only the removal of hydrogen as oxidation, but also the removal of electropositive elements as oxidation. Thus the reaction :

$$2K_4\ [Fe(CN)_6](aq) + H_2O_2\ (aq) \rightarrow 2K_3[Fe(CN)_6](aq) + 2\ KOH\ (aq)$$

is interpreted as oxidation due to the removal of electropositive element potassium from potassium ferrocyanide before it changes to potassium ferricyanide. To summarise, the term “oxidation” is defined as the addition of oxygen/electronegative element to a substance or removal of hydrogen/electropositive element from a substance.

In the beginning, reduction was considered as removal of oxygen from a compound. However, the term reduction has been broadened these days to include removal of oxygen/electronegative element from a substance or addition of hydrogen/electropositive element to a substance.

According to the definition given above, the following are the examples of reduction processes:

$2\ HgO\ (s) \xrightarrow{\Delta} 2\ Hg\ (l) + O_2\ (g)$ (8.8)

(removal of oxygen from mercuric oxide)

$2\ FeCl_3\ (aq) + H_2\ (g) \rightarrow 2\ FeCl_2\ (aq) + 2\ HCl(aq)$ (8.9)

(removal of electronegative element, chlorine from ferric chloride)

$CH_2 = CH_2\ (g) + H_2\ (g) \rightarrow H_3C - CH_3\ (g)$ (8.10)

(addition of hydrogen)

$2HgCl_2\ (aq) + SnCl_2\ (aq) \rightarrow Hg_2Cl_2\ (s) + SnCl_4\ (aq)$ (8.11)

(addition of mercury to mercuric chloride)

In reaction (8.11) simultaneous oxidation of stannous chloride to stannic chloride is also occurring because of the addition of electronegative element chlorine to it. It was soon realised that oxidation and reduction always occur simultaneously (as will be apparent by re-examining all the equations given above), hence, the word “redox” was coined for this class of chemical reactions.

Problem 8.1

In the reactions given below, identify the species undergoing oxidation and reduction:

(i) H_2S (g) + Cl_2 (g) → 2 HCl (g) + S (s)

(ii) $3Fe_3O_4$ (s) + 8 Al (s) → 9 Fe (s)

+ 4Al2O3 (s)

(iii) 2 Na (s) + H_2 (g) → 2 NaH (s)

Solution

(i) H_2S is oxidised because a more electronegative element, chlorine is added to hydrogen (or a more electropositive element, hydrogen has been removed
from S). Chlorine is reduced due to addition of hydrogen to it.

(ii) Aluminium is oxidised because oxygen is added to it. Ferrous ferric oxide (Fe_3O_4) is reduced because oxygen has been removed from it.

(iii) With the careful application of the concept of electronegativity only we may infer that sodium is oxidised and hydrogen is reduced.

Reaction (iii) chosen here prompts us to think in terms of another way to define redox reactions.

8.2 REDOX REACTIONS IN TERMS OF ELECTRON TRANSFER REACTIONS

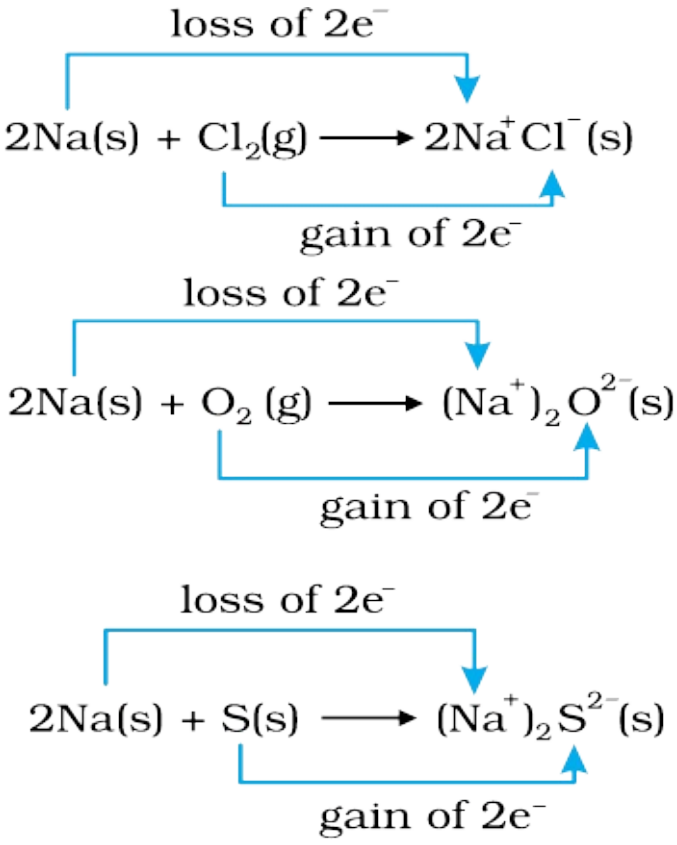
We have already learnt that the reactions

$2Na(s) + Cl_2(g) \rightarrow 2NaCl\ (s)$ (8.12)

$4Na(s) + O_2(g) \rightarrow 2Na_2O(s)$ (8.13)

$2Na(s) + S(s) \rightarrow Na_2S(s)$ (8.14)

are redox reactions because in each of these reactions sodium is oxidised due to the addition of either oxygen or more electronegative element to sodium. Simultaneously, chlorine, oxygen and sulphur are reduced because to each of these, the electropositive element sodium has been added. From our knowledge of chemical bonding we also know that sodium chloride, sodium oxide and sodium sulphide are ionic compounds and perhaps better written as Na^+Cl^- (s), $(Na^+)_2O^{2-}$(s), and $(Na^+)_2\ S^{2-}$(s). Development of charges on the species produced suggests us to rewrite the reactions (8.12 to 8.14) in the following manner :



For convenience, each of the above processes can be considered as two separate steps, one involving the loss of electrons and the other the gain of electrons. As an illustration, we may further elaborate one of these, say, the formation of sodium chloride.

$2\ Na(s) \rightarrow 2\ Na+(g)\ ^{+}\ 2e^{-}$

$Cl_2(g) + 2e\_ \rightarrow 2\ Cl^{-}(g)$

Each of the above steps is called a half reaction, which explicitly shows involvement of electrons. Sum of the half reactions gives the overall reaction :

$2\ Na(s) + Cl_2\ (g) \rightarrow 2\ Na+\ Cl^{-}\ (s)$ or $2\ NaCl\ (s)$

Reactions 8.12 to 8.14 suggest that half reactions that involve loss of electrons are called oxidation reactions. Similarly, the half reactions that involve gain of electrons are called reduction reactions. It may not be out of context to mention here that the new way of defining oxidation and reduction has been achieved only by establishing a correlation between the behaviour of species as per the classical idea and their interplay in electron-transfer change. In reactions (8.12 to 8.14) sodium, which is oxidised, acts as
a reducing agent because it donates electron to each of the elements interacting with it and thus helps in reducing them. Chlorine, oxygen and sulphur are reduced and act as oxidising agents because these accept electrons from sodium. To summarise, we may mention that

Oxidation : Loss of electron(s) by any species.

Reduction : Gain of electron(s) by any species.

Oxidising agent : Acceptor of electron(s).

Reducing agent : Donor of electron(s).

Problem 8.2 Justify that the reaction :
$2\ Na(s) + H_2(g) \rightarrow 2\ NaH\ (s)$ is a redox change.

Solution

Since in the above reaction the compound formed is an ionic compound, which may also be represented as Na+H– (s), this suggests that one half reaction in this process is :

$2\ Na\ (s) \rightarrow 2\ Na^{+}(g) + 2e^{-}$

and the other half reaction is:

$H_2\ (g) + 2e– \rightarrow 2\ H^{-}(g)$

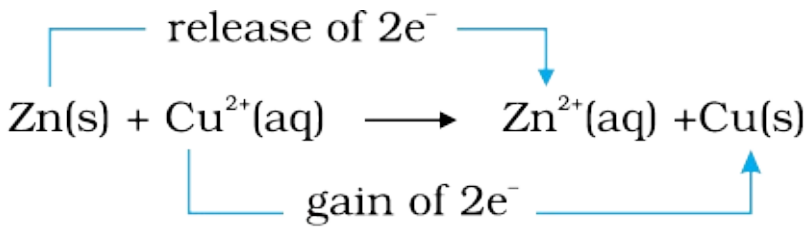
This splitting of the reaction under examination into two half reactions automatically reveals that here sodium is oxidised and hydrogen is reduced, therefore, the complete reaction is a redox change.

8.2.1 Competitive Electron Transfer Reactions

Place a strip of metallic zinc in an aqueous solution of copper nitrate as shown in Fig. 8.1, for about one hour. You may notice that the strip becomes coated with reddish metallic copper and the blue colour of the solution disappears. Formation of Zn^{2+} ions among the products can easily be judged when the blue colour of the solution due to Cu^{2+} has disappeared. If hydrogen sulphide gas is passed through the colourless solution containing Zn^{2+} ions, appearance of white zinc sulphide, ZnS can be seen on making the solution alkaline with ammonia.

The reaction between metallic zinc and the aqueous solution of copper nitrate is :

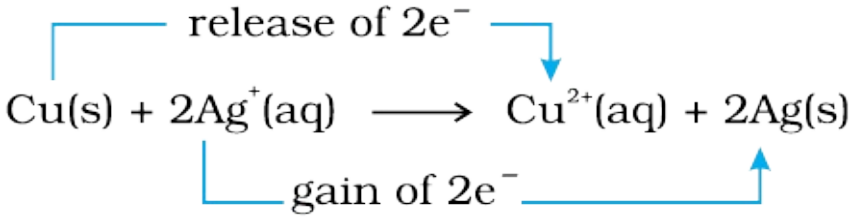
$$Zn(s) + Cu^{2+}\ (aq) \rightarrow Zn^{2+}\ (aq) + Cu(s) \qquad (8.15)$$



In reaction (8.15), zinc has lost electrons to form Zn^{2+} and, therefore, zinc is oxidised. Evidently, now if zinc is oxidised, releasing electrons, something must be reduced, accepting the electrons lost by zinc. Copper ion is reduced by gaining electrons from the zinc.

Reaction (8.15) may be rewritten as :

At this stage we may investigate the state of equilibrium for the reaction represented by equation (8.15). For this purpose, let us place a strip of metallic copper in a zinc sulphate solution. No visible reaction is noticed and attempt to detect the presence of Cu^{2+} ions by passing H_2S gas through the solution to produce the black colour of cupric sulphide, CuS, does not succeed. Cupric sulphide has such a low solubility that this is an extremely sensitive test; yet the amount of Cu^{2+} formed cannot be detected. We thus conclude that the state of equilibrium for the reaction (8.15) greatly favours the products over the reactants.



(8.16)

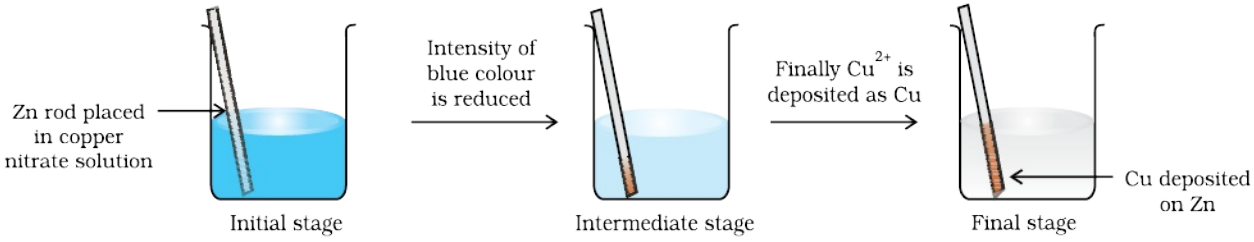
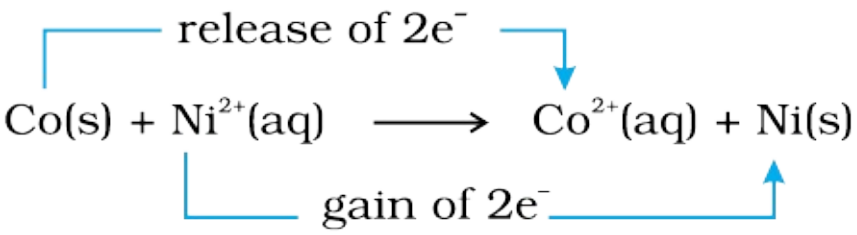


Fig. 8.1 Redox reaction between zinc and aqueous solution of copper nitrate occurring in a

beaker.



(8.17)

Let us extend electron transfer reaction now to copper metal and silver nitrate solution in water and arrange a set-up as shown in Fig. 8.2. The solution develops blue colour due to the formation of Cu^{2+} ions on account of the reaction:

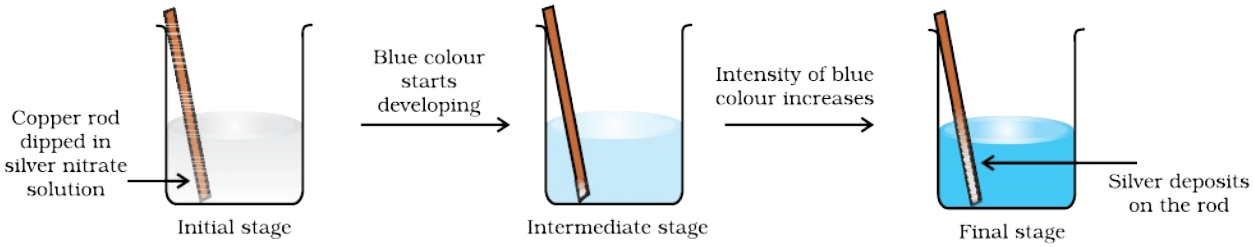


Fig. 8.2 Redox reaction between copper and aqueous solution of silver nitrate occurring in a beaker.

Here, Cu(s) is oxidised to Cu^{2+}(aq) and
Ag+(aq) is reduced to Ag(s). Equilibrium greatly favours the products Cu^{2+} (aq) and Ag(s).

By way of contrast, let us also compare the reaction of metallic cobalt placed in nickel sulphate solution. The reaction that occurs here is :

At equilibrium, chemical tests reveal that both Ni^{2+}(aq) and Co^{2+}(aq) are present at moderate concentrations. In this case, neither the reactants [Co(s) and Ni^{2+}(aq)] nor the products [Co^{2+}(aq) and Ni (s)] are greatly favoured.

This competition for release of electrons incidently reminds us of the competition for release of protons among acids. The similarity suggests that we might develop a table in which metals and their ions are listed on the basis of their tendency to release electrons just as we do in the case of acids to indicate the strength of the acids. As a matter of fact we have already made certain comparisons. By comparison we have come to know that zinc releases electrons to copper and copper releases electrons to silver and, therefore, the electron releasing tendency of the metals is in the order: Zn>Cu>Ag. We would love to make our list more vast and design a metal activity series or electrochemical series. The competition for electrons between various metals helps us to design a class of cells, named as Galvanic cells in which the chemical reactions become the source of electrical energy. We would study more about these cells in Class XII.

8.3 OXIDATION NUMBER

A less obvious example of electron transfer is realised when hydrogen combines with oxygen to form water by the reaction:

$$2H_2(g) + O_2(g) \rightarrow 2H_2O(l) \qquad (8.18)$$

Though not simple in its approach, yet we can visualise the H atom as going from a neutral (zero) state in H_2 to a positive state in H_2O, the O atom goes from a zero state in O_2 to a dinegative state in H_2O. It is assumed that there is an electron transfer from H to O and consequently H_2 is oxidised and O_2 is reduced. However, as we shall see later, the charge transfer is only partial and is perhaps better described as an electron shift rather than a complete loss of electron by H and gain by O. What has been said here with respect to equation (8.18) may be true for a good number of other reactions involving covalent compounds. Two such examples of this class of the reactions are:

$$H_2(s) + Cl_2(g) \rightarrow 2HCl(g) \quad (8.19)$$

and,

$$CH_4(g) + 4Cl_2(g) \rightarrow CCl_4(l) + 4HCl(g) \quad (8.20)$$

In order to keep track of electron shifts in chemical reactions involving formation of covalent compounds, a more practical method of using oxidation number has been developed. In this method, it is always assumed that there is a complete transfer of electron from a less electronegative atom to a more electonegative atom. For example, we rewrite equations (8.18 to 8.20) to show charge on each of the atoms forming part of the reaction :

0 0 +1 –2

$2H_2(g) + O_2(g) \rightarrow 2H_2O\ (l)$ (8.21)

0 0 +1 –1

$H_2\ (s) + Cl_2(g) \rightarrow 2HCl(g)$ (8.22)

–4+1 0 +4 –1 +1 –1

$CH_4(g) + 4Cl_2(g) \rightarrow CCl_4(l) + 4HCl(g)$ (8.23)

It may be emphasised that the assumption of electron transfer is made for book-keeping purpose only and it will become obvious at a later stage in this unit that it leads to the simple description of redox reactions.

Oxidation number denotes the oxidation state of an element in a compound ascertained according to a set of rules formulated on the basis that electron pair in a covalent bond belongs entirely to more electronegative element.

It is not always possible to remember or make out easily in a compound/ion, which element is more electronegative than the other. Therefore, a set of rules has been formulated to determine the oxidation

number of an element in a compound/ion. If two or more than two atoms of an element are present in the molecule/ion such as $Na_2S_2O_3$/Cr_2O7^{2-}, the oxidation number of the atom of that element will then be the average of the oxidation number of all the atoms of that element. We may at this stage, state the rules for the calculation of oxidation number. These rules are:

1. In elements, in the free or the uncombined state, each atom bears an oxidation number of zero. Evidently each atom in H_2, O_2, Cl_2, O_3, P_4, S_8, Na, Mg, Al has the oxidation number zero.

2. For ions composed of only one atom, the oxidation number is equal to the charge on the ion. Thus Na^+ ion has an oxidation number of +1, Mg^{2+} ion, +2, Fe^{3+} ion, +3, Cl– ion, –1, O^{2-} ion, –2; and so on. In their compounds all alkali metals have oxidation number of +1, and all alkaline earth metals have an oxidation number of +2. Aluminium is regarded to have an oxidation number of +3 in all its compounds.

3. The oxidation number of oxygen in most compounds is –2. However, we come across two kinds of exceptions here. One arises in the case of peroxides and superoxides, the compounds of oxygen in which oxygen atoms are directly linked to each other. While in peroxides (e.g., H_2O_2, Na_2O_2), each oxygen atom is assigned an oxidation number of –1, in superoxides (e.g., KO_2, RbO_2) each oxygen atom is assigned an oxidation number of –(½). The second exception appears rarely, i.e. when oxygen is bonded to fluorine. In such compounds e.g., oxygen difluoride (OF_2) and dioxygen difluoride (O_2F_2), the oxygen is assigned an oxidation number of +2 and +1, respectively. The number assigned to oxygen will depend upon the bonding state of oxygen but this number would now be a positive figure only.

4. The oxidation number of hydrogen is +1, except when it is bonded to

metals in binary compounds (that is compounds containing two elements). For example, in LiH, NaH, and CaH_2, its oxidation number is –1.

5. In all its compounds, fluorine has an oxidation number of –1. Other halogens (Cl, Br, and I) also have an oxidation number of –1, when they occur as halide ions in their compounds. Chlorine, bromine and iodine when combined with oxygen, for example in oxoacids and oxoanions, have positive oxidation numbers.

6. The algebraic sum of the oxidation number of all the atoms in a compound must be zero. In polyatomic ion, the algebraic sum of all the oxidation numbers of atoms of the ion must equal the charge on the ion. Thus, the sum of oxidation number of three oxygen atoms and one carbon atom in the carbonate ion, $(CO_3)^{2-}$ must equal –2.

By the application of above rules, we can find out the oxidation number of the desired element in a molecule or in an ion. It is clear that the metallic elements have positive oxidation number and nonmetallic elements have positive or negative oxidation number. The atoms of transition elements usually display several positive oxidation states. The highest oxidation number of a representative element is the group number for the first two groups and the group number minus 10 (following the long form of periodic table) for the other groups. Thus, it implies that the highest value of oxidation number exhibited by an atom of an element generally increases across the period in the periodic table. In the third period, the highest value of oxidation number changes from 1 to 7 as indicated below in the compounds of the elements.

Group	**1**	**2**	**13**	**14**	**15**	**16**	**17**
Element	Na	Mg	Al	Si	P	S	Cl

Compound	NaCl	$MgSO_4$	AlF_3	$SiCl_4$	P_4O_{10}	SF_6	$HClO_4$
Highest oxidation number state of the group element	+1	+2	+3	+4	+5	+6	+7

A term that is often used interchangeably with the oxidation number is the oxidation state. Thus in CO_2, the oxidation state of carbon is +4, that is also its oxidation number and similarly the oxidation state as well as oxidation number of oxygen is – 2. This implies that the oxidation number denotes the oxidation state of an element in a compound. The oxidation number/state of a metal in a compound is sometimes presented according to the notation given by German chemist, Alfred Stock. It is popularly known as Stock notation. According to this, the oxidation number is expressed by putting a Roman numeral representing the oxidation number in parenthesis after the symbol of the metal in the molecular formula. Thus aurous chloride and auric chloride are written as Au(I)Cl and $Au(III)Cl_3$. Similarly, stannous chloride and stannic chloride are written as $Sn(II)Cl_2$ and $Sn(IV)Cl_4$. This change in oxidation number implies change in oxidation state, which in turn helps to identify whether the species is present in oxidised form or reduced form. Thus, $Hg_2(I)Cl_2$ is the reduced form of $Hg(II)\ Cl_2$.

Problem 8.3

Using Stock notation, represent the following compounds :HAuCl4, Tl_2O, FeO, Fe_2O_3, CuI, CuO, MnO and MnO_2.

Solution

By applying various rules of calculating the oxidation number of the desired element in a compound, the oxidation number of each metallic element in its compound is as follows:

$HAuCl_4$ → Au has 3

Tl_2O → Tl has 1

FeO → Fe has 2

Fe_2O_3 → Fe has 3

CuI → Cu has 1

CuO → Cu has 2

MnO → Mn has 2

MnO_2 → Mn has 4

Therefore, these compounds may be represented as:

$HAu(III)Cl_4$, $Tl_2(I)O$, $Fe(II)O$, $Fe_2(III)O_3$, $Cu(I)I$, $Cu(II)O$, $Mn(II)O$, $Mn(IV)O_2$.

The idea of oxidation number has been invariably applied to define oxidation, reduction, oxidising agent (oxidant), reducing agent (reductant) and the redox reaction. To summarise, we may say that:

Oxidation: An increase in the oxidation number of the element in the given substance.

Reduction : A decrease in the oxidation number of the element in the given substance.

Oxidising agent: A reagent which can increase the oxidation number of an element in a given substance. These reagents are called as oxidants also.

Reducing agent: A reagent which lowers the oxidation number of an

element in a given substance. These reagents are also called as reductants.

Redox reactions: Reactions which involve change in oxidation number of the interacting species.

Problem 8.4

Justify that the reaction:

$2Cu_2O(s) + Cu_2S(s) \rightarrow 6Cu(s) + SO_2(g)$

is a redox reaction. Identify the species oxidised/reduced, which acts as an oxidant and which acts as a reductant.

Solution

Let us assign oxidation number to each of the species in the reaction under examination. This results into:

+1 –2 +1 –2 0 +4 –2

$2Cu_2O(s) + Cu_2S(s) \rightarrow 6Cu(s) + SO_2$

We therefore, conclude that in this reaction copper is reduced from +1 state to zero oxidation state and sulphur is oxidised from –2 state to +4 state. The above reaction is thus a redox reaction. Further, Cu_2O helps sulphur in Cu_2S to increase its oxidation number, therefore, Cu(I) is an oxidant; and sulphur of Cu_2S helps copper both in Cu_2S itself and Cu_2O to decrease its oxidation number; therefore, sulphur of Cu_2S is reductant.

8.3.1 Types of Redox Reactions

1. Combination reactions

A combination reaction may be denoted in the manner:

$A + B \rightarrow C$

Either A and B or both A and B must be in the elemental form for such a reaction to be a redox reaction. All combustion reactions, which make use of elemental dioxygen, as well as other reactions involving elements other than dioxygen, are redox reactions. Some important examples of this category are:

0 0 +4 –2

$$C(s) + O_2(g) \xrightarrow{\Delta} CO_2(g) \quad (8.24)$$

0 0 +2 –3

$$3Mg(s) + N_2(g) \xrightarrow{\Delta} Mg_3N_2(s) \quad (8.25)$$

–4+1 0 +4 –2 +1 –2

$$CH_4(g) + 2O_2(g) \xrightarrow{\Delta} CO_2(g) + 2H_2O\ (l)$$

2. Decomposition reactions

Decomposition reactions are the opposite of combination reactions. Precisely, a decomposition reaction leads to the breakdown of a compound into two or more components at least one of which must be in the elemental state. Examples of this class of reactions are:

+1 –2 0 0

$$2H_2O\ (l) \xrightarrow{\Delta} 2H_2\ (g) + O_2(g) \quad (8.26)$$

+1 –1 0 0

$$2NaH\ (s) \xrightarrow{\Delta} 2Na\ (s) + H_2(g) \quad (8.27)$$

+1 +5 –2 +1 –1 0

$$2KClO_3\ (s) \xrightarrow{\Delta} 2KCl\ (s) + 3O_2(g) \quad (8.28)$$

It may carefully be noted that there is no change in the oxidation number of hydrogen in methane under combination reactions and that of

potassium in potassium chlorate in reaction (8.28). This may also be noted here that all decomposition reactions are not redox reactions. For example, decomposition of calcium carbonate is not a redox reaction.

+2 +4 –2 +2 –2 +4 –2

$CaCO_3(s) \xrightarrow{\Delta} CaO(s) + CO_2(g)$

3. Displacement reactions

In a displacement reaction, an ion (or an atom) in a compound is replaced by an ion (or an atom) of another element. It may be denoted as:

$$X + YZ \rightarrow XZ + Y$$

Displacement reactions fit into two categories: metal displacement and non-metal displacement.

(a) Metal displacement: A metal in a compound can be displaced by another metal in the uncombined state. We have already discussed about this class of the reactions under section 8.2.1. Metal displacement reactions find many applications in metallurgical processes in which pure metals are obtained from their compounds in ores. A few such examples are:

+2+6–2 0 0 +2 +6 –2

$CuSO_4(aq) + Zn(s) \rightarrow Cu(s) + ZnSO_4(aq)$ (8.29)

+5 –2 0 0 +2 –2

$V_2O_5(s) + 5Ca(s \xrightarrow{\Delta} 2V(s) + 5CaO(s)$

(8.30)

+4 –1 0 0 +2 –1

$TiCl_4(l) + 2Mg(s \xrightarrow{\Delta} Ti(s) + 2\,MgCl_2(s)$

(8.31)

+3 –2 0 +3 –2 0

Cr_2O_3 (s) + 2 Al (s) $\xrightarrow{\Delta}$ Al_2O_3 (s) + 2Cr(s) (8.32)

In each case, the reducing metal is a better reducing agent than the one that is being reduced which evidently shows more capability to lose electrons as compared to the one that is reduced.

(b) Non-metal displacement: The non-metal displacement redox reactions include hydrogen displacement and a rarely occurring reaction involving oxygen displacement.

All alkali metals and some alkaline earth metals (Ca, Sr, and Ba) which are very good reductants, will displace hydrogen from cold water.

0 +1 –2 +1 –2 +1 0

$2Na(s) + 2H_2O(l) \rightarrow 2NaOH(aq) + H_2(g)$ (8.33)

0 +1 –2 +2 –2 +1 0

$Ca(s) + 2H_2O(l) \rightarrow Ca(OH)_2(aq) + H_2(g)$ (8.34)

Less active metals such as magnesium and iron react with steam to produce dihydrogen gas:

0 +1 –2 +2 –2 +1 0

$Mg(s) + 2H_2O(l) \xrightarrow{\Delta} Mg(OH)_2(s) + H_2(g)$

(8.35)

0 +1 –2 +3 –2 0

$2Fe(s) + 3H_2O(l) \xrightarrow{\Delta} Fe_2O_3(s) + 3H_2(g)$ (8.36)

Many metals, including those which do not react with cold water, are capable of displacing hydrogen from acids. Dihydrogen from acids may

even be produced by such metals which do not react with steam. Cadmium and tin are the examples of such metals. A few examples for the displacement of hydrogen from acids are:

0 +1 –1 +2 –1 0

$$Zn(s) + 2HCl(aq) \rightarrow ZnCl_2\ (aq) + H_2\ (g) \qquad (8.37)$$

0 +1 –1 +2 –1 0

$$Mg\ (s) + 2HCl\ (aq) \rightarrow MgCl_2\ (aq) + H_2\ (g) \qquad (8.38)$$

0 +1 –1 +2 –1 0

$$Fe(s) + 2HCl(aq) \rightarrow FeCl_2(aq) + H_2(g) \qquad (8.39)$$

Reactions (8.37 to 8.39) are used to prepare dihydrogen gas in the laboratory. Here, the reactivity of metals is reflected in the rate of hydrogen gas evolution, which is the slowest for the least active metal Fe, and the fastest for the most reactive metal, Mg. Very less active metals, which may occur in the native state such as silver (Ag), and gold (Au) do not react even with hydrochloric acid.

In section (8.2.1) we have already discussed that the metals – zinc (Zn), copper (Cu) and silver (Ag) through tendency to lose electrons show their reducing activity in the order Zn> Cu>Ag. Like metals, activity series also exists for the halogens. The power of these elements as oxidising agents decreases as we move down from fluorine to iodine in group 17 of the periodic table. This implies that fluorine is so reactive that it can replace chloride, bromide and iodide ions in solution. In fact, fluorine is so reactive that it attacks water and displaces the oxygen of water :

+1 –2 0 +1 –1 0

$$2H_2O\ (l) + 2F_2\ (g) \rightarrow 4HF(aq) + O_2(g) \qquad (8.40)$$

It is for this reason that the displacement reactions of chlorine, bromine

and iodine using fluorine are not generally carried out in aqueous solution. On the other hand, chlorine can displace bromide and iodide ions in an aqueous solution as shown below:

0 +1 –1 +1 –1 0

Cl_2 (g) + 2KBr (aq) → 2 KCl (aq) + Br_2 (l) (8.41)

0 +1–1 +1 –1 0

Cl_2 (g) + 2KI (aq) → 2 KCl (aq) + I_2 (s) (8.42)

As Br_2 and I_2 are coloured and dissolve in CCl_4, can easily be identified from the colour of the solution. The above reactions can be written in ionic form as:

0 –1 –1 0

Cl_2 (g) + $2Br^-$ (aq) → $2Cl^-$ (aq) + Br_2 (l) (8.41a)

0 –1 –1 0

Cl_2 (g) + $2I^-$ (aq) → $2Cl^-$ (aq) + I_2 (s) (8.42b)

Reactions (8.41) and (8.42) form the basis of identifying Br– and I– in the laboratory through the test popularly known as ‘Layer Test’. It may not be out of place to mention here that bromine likewise can displace iodide ion in solution:

0 –1 –1 0

Br_2 (l) + $2I^-$ (aq) → $2Br^-$ (aq) + I_2 (s) (8.43)

The halogen displacement reactions have a direct industrial application. The recovery of halogens from their halides requires an oxidation process, which is represented by:

$2X^- \rightarrow X_2 + 2e^-$ (8.44)

here X denotes a halogen element. Whereas chemical means are

available to oxidise Cl^-, Br^- and I^-, as fluorine is the strongest oxidising agent; there is no way to convert F^- ions to F_2 by chemical means. The only way to achieve F_2 from F^- is to oxidise electrolytically, the details of which you will study at a later stage.

4. DISPROPORTIONATION REACTIONS

Disproportionation reactions are a special type of redox reactions. In a disproportionation reaction an element in one oxidation state is simultaneously oxidised and reduced. One of the reacting substances in a disproportionation reaction always contains an element that can exist in at least three oxidation states. The element in the form of reacting substance is in the intermediate oxidation state; and both higher and lower oxidation states of that element are formed in the reaction. The decomposition of hydrogen peroxide is a familiar example of the reaction, where oxygen experiences disproportionation.

+1 –1 +1 –2 0

$$2H_2O_2\,(aq) \rightarrow 2H_2O(l) + O_2(g) \qquad (8.45)$$

Here the oxygen of peroxide, which is present in –1 state, is converted to zero oxidation state in O_2 and decreases to –2 oxidation state in H_2O.

Phosphorous, sulphur and chlorine undergo disproportionation in the alkaline medium as shown below :

0 –3 +1

$$P_4(s) + 3OH{-}(aq) + 3H_2O(l) \rightarrow PH_3(g) + 3H2PO_2^-\,(aq) \qquad (8.46)$$

0 –2 +2

$$S_8(s) + 12OH^-\,(aq) \rightarrow 4S^{2-}\,(aq) + 2S_2O_3^{2-}(aq) + 6H_2O(l) \qquad (8.47)$$

0 +1 –1

Cl_2 (g) + 2OH^- (aq) → ClO^- (aq) + Cl^- (aq) + H_2O (l) (8.48)

The reaction (8.48) describes the formation of household bleaching agents. The hypochlorite ion (ClO^-) formed in the reaction oxidises the colour-bearing stains of the substances to colourless compounds.

It is of interest to mention here that whereas bromine and iodine follow the same trend as exhibited by chlorine in reaction (8.48), fluorine shows deviation from this behaviour when it reacts with alkali. The reaction that takes place in the case of fluorine is as follows:

2 F_2(g) + 2OH^-(aq) → 2 F^-(aq) + OF_2(g) + H_2O(l) (8.49)

(It is to be noted with care that fluorine in reaction (8.49) will undoubtedly attack water to produce some oxygen also). This departure shown by fluorine is not surprising for us as we know the limitation of fluorine that, being the most electronegative element, it cannot exhibit any positive oxidation state. This means that among halogens, fluorine does not show a disproportionation tendency.

Problem 8.5

Which of the following species, do not show disproportionation reaction and why ?

ClO–, ClO_2^-, ClO_3– and ClO_4^-

Also write reaction for each of the species that disproportionates.

Solution

Among the oxoanions of chlorine listed above, ClO_4^- does not disproportionate because in this oxoanion chlorine is present in its highest oxidation state that is, +7. The disproportionation reactions for the other three oxoanions of chlorine are as follows:

+1 –1 +5

$3ClO^- \rightarrow 2Cl^- + ClO_3^-$

+3 +5 –1

$6\ ClO_2^- \xrightarrow{h\nu} 4ClO_3^- + 2Cl^-$

+5 –1 +7

$4ClO_3^- \rightarrow Cl^- + 3\ ClO_4^-$

Problem 8.6

Suggest a scheme of classification of the following redox reactions

(a) $N_2\ (g) + O_2\ (g) \rightarrow 2\ NO\ (g)$

(b) $2Pb(NO_3)_2(s) \rightarrow 2PbO(s) + 4\ NO2\ (g) + O2\ (g)$

(c) $NaH(s) + H_2O(l) \rightarrow NaOH(aq) + H_2\ (g)$

(d) $2NO_2(g) + 2OH^-(aq) \rightarrow NO_2^-(aq) + NO_3^-\ (aq) + H2O(l)$

Solution

In reaction (a), the compound nitric oxide is formed by the combination of the elemental substances, nitrogen and oxygen; therefore, this is an example of combination redox reactions. The reaction (b) involves the breaking down of lead nitrate into three components; therefore, this is categorised under decomposition redox reaction. In reaction (c), hydrogen of water has been displaced by hydride ion into dihydrogen gas. Therefore, this may be called as displacement redox reaction. The reaction (d) involves disproportionation of NO2
(+4 state) into NO2– (+3 state) and NO3– (+5 state). Therefore reaction (d) is an example of disproportionation redox reaction.

The Paradox of Fractional Oxidation Number

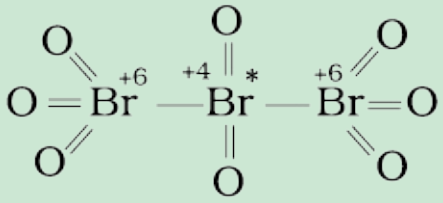
Sometimes, we come across with certain compounds in which the oxidation number of a particular element in the compound is in fraction. Examples are:

C_3O_2 [where oxidation number of carbon is (4/3)],

Br_3O_8 [where oxidation number of bromine is (16/3)]

and $Na_2S_4O_6$ (where oxidation number of sulphur is 2.5).

We know that the idea of fractional oxidation number is unconvincing to us, because electrons are never shared/transferred in fraction. Actually this fractional oxidation state is the average oxidation state of the element under examination and the structural parameters reveal that the element for whom fractional oxidation state is realised is present in different oxidation states. Structure of the species C_3O_2, Br_3O_8 and $S_4O_6^{2-}$ reveal the following bonding situations:



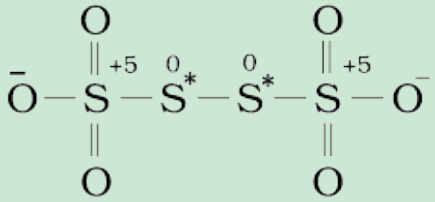
Structure of Br_3O_8 (tribromooctaoxide)

+2 0 +2

O = C = C*= C = O

Structure of C_3O_2

(carbon suboxide)



Structure of $S_4O_6^{2-}$ (tetrathionate ion)

The element marked with asterisk in each species is exhibiting the different oxidation state (oxidation number) from rest of the atoms of the same element in each of the species. This reveals that in C_3O_2, two carbon atoms are present in +2 oxidation state each, whereas the third one is present in zero oxidation state and the average is 4/3. However, the realistic picture is +2 for two terminal carbons and zero for the middle carbon. Likewise in Br_3O_8, each of the two terminal

bromine atoms are present in +6 oxidation state and the middle bromine is present in +4 oxidation state. Once again the average, that is different from reality, is
16/3. In the same fashion, in the species $S_4O_6^{2-}$, each of the two extreme sulphurs exhibits oxidation state of +5 and the two middle sulphurs as zero. The average of four oxidation numbers of sulphurs of the $S_4O_6^{2-}$ is 2.5, whereas the reality being + 5,0,0 and +5 oxidation number respectively for each sulphur.

We may thus, in general, conclude that the idea of fractional oxidation state should be taken with care and the reality is revealed by the structures only. Further, whenever we come across with fractional oxidation state of any particular element in any species, we must understand that this is the average oxidation number only. In reality (revealed by structures only), the element in that particular species is present in more than one whole number oxidation states. Fe_3O_4, Mn3O4, Pb_3O_4 are some of the other examples of the compounds, which are mixed oxides, where we come across with fractional oxidation states of the metal atom. However, the oxidation states may be in fraction as in O_2^+ and O_2^- where it is +½ and –½ respectively.

Problem 8.7

Why do the following reactions proceed differently ?

$Pb_3O_4 + 8HCl \rightarrow 3PbCl_2 + Cl_2 + 4H_2O$ and

$Pb_3O_4 + 4HNO_3 \rightarrow 2Pb(NO_3)_2 + PbO_2 + 2H_2O$

Solution

Pb_3O_4 is actually a stoichiometric mixture of 2 mol of PbO and 1 mol of PbO_2. In PbO_2, lead is present in +4 oxidation state, whereas the stable oxidation state of lead in PbO is +2. PbO_2 thus can act as an oxidant (oxidising agent) and, therefore, can oxidise Cl– ion of HCl into chlorine. We may also keep in mind that PbO is a basic oxide. Therefore, the reaction

$Pb_3O_4 + 8HCl \rightarrow 3PbCl_2 + Cl_2 + 4H_2O$

can be splitted into two reactions namely:

$2PbO + 4HCl \rightarrow 2PbCl_2 + 2H_2O$

(acid-base reaction)

+4 –1 +2 0

$PbO_2 + 4HCl \rightarrow PbCl_2 + Cl_2 + 2H_2O$ (redox reaction)

Since HNO_3 itself is an oxidising agent therefore, it is unlikely that the reaction may occur between PbO_2 and HNO_3. However, the acid-base reaction occurs between PbO and HNO_3 as:

$2PbO + 4HNO_3 \rightarrow 2Pb(NO_3)_2 + 2H_2O$

It is the passive nature of PbO_2 against HNO_3 that makes the reaction different from the one that follows with HCl.

8.3.2 Balancing of Redox Reactions

Two methods are used to balance chemical equations for redox processes. One of these methods is based on the change in the oxidation number of reducing agent and the oxidising agent and the other method is based on splitting the redox reaction into two half reactions — one involving oxidation and the other involving reduction. Both these methods are in use and the choice of their use rests with the individual using them.

(a) Oxidation Number Method: In writing equations for oxidation-reduction reactions, just as for other reactions, the compositions and formulas must be known for the substances that react and for the products that are formed. The oxidation number method is now best illustrated in the following steps:

Step 1: Write the correct formula for each reactant and product.

Step 2: Identify atoms which undergo change in oxidation number in the reaction by assigning the oxidation number to all elements in the reaction.

Step 3: Calculate the increase or decrease in the oxidation number per atom and for the entire molecule/ion in which it occurs. If these are not equal then multiply by suitable number so that these become equal. (If you realise that two substances are reduced and nothing is oxidised or vice-versa, something is wrong. Either the formulas of reactants or products are wrong or the oxidation numbers have not been assigned properly).

Step 4: Ascertain the involvement of ions if the reaction is taking place in water, add H^+ or OH^- ions to the expression on the appropriate side so that the total ionic charges of reactants and products are equal. If the reaction is carried out in acidic solution, use H+ ions in the equation; if in basic solution, use OH^- ions.

Step 5: Make the numbers of hydrogen atoms in the expression on the two sides equal by adding water (H_2O) molecules to the reactants or products. Now, also check the number of oxygen atoms. If there are the same number of oxygen atoms in the reactants and products, the equation then represents the balanced redox reaction.

Let us now explain the steps involved in the method with the help of a few problems given below:

Problem 8.8

Write the net ionic equation for the reaction of potassium dichromate(VI), $K_2Cr_2O_7$ with sodium sulphite, Na_2SO_3, in an acid

solution to give chromium(III) ion and the sulphate ion.

Solution

Step 1: The skeletal ionic equation is:

$Cr_2O_7^{2-}(aq) + SO_3^{2-}(aq) \rightarrow Cr^{3+}(aq) + SO_4^{2-}(aq)$

Step 2: Assign oxidation numbers for Cr and S

+6 –2 +4 –2 +3 +6 –2

$Cr_2O_7^{2-}(aq) + SO_3^{2-}(aq) \rightarrow Cr(aq) + SO_4^{2-}(aq)$

This indicates that the dichromate ion is the oxidant and the sulphite ion is the reductant.

Step 3: Calculate the increase and decrease of oxidation number, and make them equal: from step-2 we can notice that there is change in oxidation state of chromium and sulphur. Oxidation state of chromium changes form +6 to +3. There is decrease of +3 in oxidation state of chromium on right hand side of the equation. Oxidation state of sulphur changes from +4 to +6. There is an increase of +2 in the oxidation state of sulphur on right hand side. To make the increase and decrease of oxidation state equal, place numeral 2 before cromium ion on right hand side and numeral 3 before sulphate ion on right hand side and balance the chromium and sulphur atoms on both the sides of the equation. Thus we get

+6 –2 +4 –2 +3 +6 –2

$Cr_2O_7^{2-}(aq) + 3SO_3^{2-}(aq) \rightarrow 2Cr^{3+}(aq) + 3SO_4^{2-}(aq)$

Step 4: As the reaction occurs in the acidic medium, and further the ionic charges are not equal on both the sides, add 8H+ on the left to make ionic charges equal

$Cr_2O_7^{2-}(aq) + 3SO_3^{2-}(aq) + 8H^+ \rightarrow 2Cr^{3+}(aq) + 3SO_4^{2-}(aq)$

Step 5: Finally, count the hydrogen atoms, and add appropriate number of water molecules (i.e., 4H2O) on the right to achieve balanced redox change.

$Cr_2O_7^{2-}(aq) + 3SO_3^{2-}(aq) + 8H^+(aq) \rightarrow 2Cr^{3+}(aq) + 3SO_4^{2-}(aq)$

$+4H_2O$ (l)

Problem 8.9

Permanganate ion reacts with bromide ion in basic medium to give manganese dioxide and bromate ion. Write the balanced ionic equation for the reaction.

Solution

Step 1: The skeletal ionic equation is :

$MnO_4^-(aq) + Br^-(aq) \rightarrow MnO_2(s) + BrO_3^-(aq)$

Step 2: Assign oxidation numbers for Mn and Br

+7 –1 +4 +5

$MnO_4^-(aq) + Br^-(aq) \rightarrow MnO_2(s) + BrO_3^-(aq)$

this indicates that permanganate ion is the oxidant and bromide ion is the reductant.

Step 3: Calculate the increase and decrease of oxidation number, and make the increase equal to the decrease.

+7 –1 +4 +5

$2MnO_4^-(aq) + Br^-(aq) \rightarrow 2MnO_2(s) + BrO_3^-(aq)$

Step 4: As the reaction occurs in the basic medium, and the ionic charges are not equal on both sides, add 2 OH– ions on the right to make ionic charges equal.

$2MnO_4^-(aq) + Br^-(aq) \rightarrow 2MnO_2(s) + BrO_3^-(aq) + 2OH^-(aq)$

Step 5: Finally, count the hydrogen atoms and add appropriate number of water molecules (i.e. one H_2O molecule) on the left side to achieve balanced redox change.

$2MnO_4^-(aq) + Br^-(aq) + H_2O(l) \rightarrow 2MnO_2(s) + BrO_3^-(aq) + 2OH^-(aq)$

(b) Half Reaction Method: In this method, the two half equations are

balanced separately and then added together to give balanced equation.

Suppose we are to balance the equation showing the oxidation of Fe^{2+} ions to Fe^{3+} ions by dichromate ions $(Cr_2O_7)^{2-}$ in acidic medium, wherein, $Cr_2O_7^{2-}$ ions are reduced to Cr3+ ions. The following steps are involved in this task.

Step 1: Produce unbalanced equation for the reaction in ionic form :

$Fe^{2+}(aq) + Cr_2O_7^{2-}(aq) \rightarrow Fe^{3+}(aq) + Cr^{3+}(aq)$ (8.50)

Step 2: Separate the equation into half-reactions:

+2 +3

Oxidation half : $Fe^{2+}(aq) \rightarrow Fe^{3+}(aq)$ (8.51)

+6 –2 +3

Reduction half : $Cr_2O_7^{2-}(aq) \rightarrow Cr^{3+}(aq)$ (8.52)

Step 3: Balance the atoms other than O and H in each half reaction individually. Here the oxidation half reaction is already balanced with respect to Fe atoms. For the reduction half reaction, we multiply the Cr^{3+} by 2 to balance Cr atoms.

$Cr_2O_7^{2-}(aq) \rightarrow 2Cr^{3+}(aq)$ (8.53)

Step 4: For reactions occurring in acidic medium, add H_2O to balance O atoms and H^+ to balance H atoms.

Thus, we get :

$Cr_2O_7^{2-}(aq) + 14H^+(aq) \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$ (8.54)

Step 5: Add electrons to one side of the half reaction to balance the charges. If need be, make the number of electrons equal in the two half reactions by multiplying one or both half reactions by appropriate number.

The oxidation half reaction is thus rewritten to balance the charge:

Fe^{2+} (aq) → Fe^{3+} (aq) + e^- (8.55)

Now in the reduction half reaction there are net twelve positive charges on the left hand side and only six positive charges on the right hand side. Therefore, we add six electrons on the left side.

$Cr_2O_7^{2-}$ (aq) + 14H^+ (aq) + 6e^- → 2Cr^{3+}(aq) + 7H_2O (l) (8.56)

To equalise the number of electrons in both the half reactions, we multiply the oxidation half reaction by 6 and write as :

6Fe^{2+} (aq) → 6Fe^{3+}(aq) + 6e^- (8.57)

Step 6: We add the two half reactions to achieve the overall reaction and cancel the electrons on each side. This gives the net ionic equation as :

6Fe^{2+}(aq) + $Cr_2O_7^{2-}$(aq) + 14H^+(aq) → 6 Fe^{3+}(aq) + 2Cr^{3+}(aq) + 7H_2O(l) (8.58)

Step 7: Verify that the equation contains the same type and number of atoms and the same charges on both sides of the equation. This last check reveals that the equation is fully balanced with respect to number of atoms and the charges.

For the reaction in a basic medium, first balance the atoms as is done in acidic medium. Then for each H^+ ion, add an equal number of OH^- ions to both sides of the equation. Where H^+ and OH^- appear on the same side of the equation, combine these to give H_2O.

Problem 8.10

Permanganate(VII) ion, MnO_4^- in basic solution oxidises iodide ion, I^- to produce molecular iodine (I_2) and manganese (IV) oxide (MnO_2). Write a balanced ionic equation to represent this redox reaction.

Solution

Step 1: First we write the skeletal ionic equation, which is

MnO_4^- (aq) + I^- (aq) → MnO_2(s) + I_2(s)

Step 2: The two half-reactions are:

–1 0

Oxidation half : I^-(aq) → I_2 (s)

+7 +4

Reduction half: MnO_4^-(aq) → MnO_2(s)

Step 3: To balance the I atoms in the oxidation half reaction, we rewrite it as:

$2I^-$ (aq) → I_2 (s)

Step 4: To balance the O atoms in the reduction half reaction, we add two water molecules on the right:

MnO_4^- (aq) → MnO_2 (s) + 2 H_2O (l)

To balance the H atoms, we add four H+ ions on the left:

MnO_4^- (aq) + 4 H^+ (aq) → MnO_2(s) + 2H_2O (l)

As the reaction takes place in a basic solution, therefore, for four H^+ ions, we add four OH^- ions to both sides of the equation:

MnO_4^- (aq) + 4H^+ (aq) + 4OH^-(aq) → MnO_2 (s) + 2 H_2O(l) + 4OH^- (aq)

Replacing the H^+ and OH^- ions with water, the resultant equation is:

MnO_4^- (aq) + 2H_2O (l) → MnO_2 (s) + 4 OH^- (aq)

Step 5: In this step we balance the charges of the two half-reactions in the manner depicted as:

$2I^-$ (aq) → I_2 (s) + $2e^-$

MnO_4^-(aq) + 2H_2O(l) + $3e^-$ → MnO_2(s) + 4OH^-(aq)

Now to equalise the number of electrons, we multiply the oxidation half-reaction by 3 and the reduction half-reaction by 2.

$6I^-(aq) \rightarrow 3I_2(s) + 6e^-$

$2\ MnO_4^-(aq) + 4H_2O(l) + 6e^- \rightarrow 2MnO_2(s) + 8OH^-(aq)$

Step 6: Add two half-reactions to obtain the net reactions after cancelling electrons on both sides.

$6I^-(aq) + 2MnO_4^-(aq) + 4H_2O(l) \rightarrow 3I_2(s) + 2MnO_2(s) + 8OH^-(aq)$

Step 7: A final verification shows that the equation is balanced in respect of the number of atoms and charges on both sides.

8.3.3 Redox Reactions as the Basis for Titrations

In acid-base systems we come across with a titration method for finding out the strength of one solution against the other using a pH sensitive indicator. Similarly, in redox systems, the titration method can be adopted to determine the strength of a reductant/oxidant using a redox sensitive indicator. The usage of indicators in redox titration is illustrated below:

(i) In one situation, the reagent itself is intensely coloured, e.g., permanganate ion, MnO_4^-. Here MnO_4^- acts as the self indicator. The visible end point in this case is achieved after the last of the reductant (Fe^{2+} or $C_2O_4^{2-}$) is oxidised and the first lasting tinge of pink colour appears at MnO_4^- concentration as low as 10^{-6} mol dm^{-3} (10^{-6} mol L^{-1}). This ensures a minimal 'overshoot' in colour beyond the equivalence point, the point where the reductant and the oxidant are equal in terms of their mole stoichiometry.

(ii) If there is no dramatic auto-colour change (as with MnO_4^- titration), there are indicators which are oxidised immediately after the last bit of the reactant is consumed, producing a dramatic colour change. The best

example is afforded by $Cr_2O_7^{2-}$, which is not a self-indicator, but oxidises the indicator substance diphenylamine just after the equivalence point to produce an intense blue colour, thus signalling the end point.

(iii) There is yet another method which is interesting and quite common. Its use is restricted to those reagents which are able to oxidise I– ions, say, for example, Cu(II):

$$2Cu^{2+}(aq) + 4I^{-}(aq) \rightarrow Cu_2I_2(s) + I_2(aq) \quad (8.59)$$

This method relies on the facts that iodine itself gives an intense blue colour with starch and has a very specific reaction with thiosulphate ions (S2O32–), which too is a redox reaction:

$$I_2(aq) + 2\ S_2O_3^{2-}(aq) \rightarrow 2I^{-}(aq) + S_4O_6^{2-}(aq) \quad (8.60)$$

I_2, though insoluble in water, remains in solution containing KI as KI_3.

On addition of starch after the liberation of iodine from the reaction of Cu^{2+} ions on iodide ions, an intense blue colour appears. This colour disappears as soon as the iodine is consumed by the thiosulphate ions. Thus, the end-point can easily be tracked and the rest is the stoichiometric calculation only.

8.3.4 Limitations of Concept of Oxidation Number

As you have observed in the above discussion, the concept of redox processes has been evolving with time. This process of evolution is continuing. In fact, in recent past the oxidation process is visualised as a decrease in electron density and reduction process as an increase in electron density around the atom(s) involved in the reaction.

8.4 REDOX REACTIONS AND ELECTRODE PROCESSES

The experiment corresponding to reaction (8.15), can also be observed if

zinc rod is dipped in copper sulphate solution. The redox reaction takes place and during the reaction, zinc is oxidised to zinc ions and copper ions are reduced to metallic copper due to direct transfer of electrons from zinc to copper ion. During this reaction heat is also evolved. Now we modify the experiment in such a manner that for the same redox reaction transfer of electrons takes place indirectly. This necessitates the separation of zinc metal from copper sulphate solution. We take copper sulphate solution in a beaker and put a copper strip or rod in it. We also take zinc sulphate solution in another beaker and put a zinc rod or strip in it. Now reaction takes place in either of the beakers and at the interface of the metal and its salt solution in each beaker both the reduced and oxidized forms of the same species are present. These represent the species in the reduction and oxidation half reactions. A **redox couple** is defined as having together the oxidised and reduced forms of a substance taking part in an oxidation or reduction half reaction.

This is represented by separating the oxidised form from the reduced form by a vertical line or a slash representing an interface (e.g. solid/solution). For example in this experiment the two

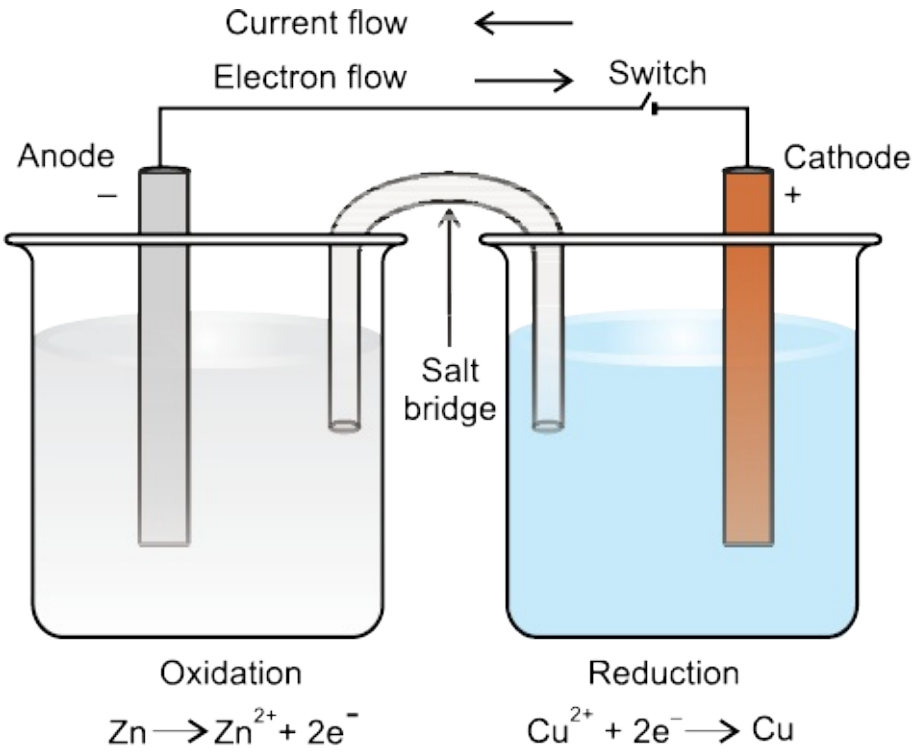


Fig. 8.3 The set-up for Daniell cell. Electrons produced at the anode due to oxidation of Zn travel through the external circuit to the cathode where these reduce the copper ions. The circuit is completed inside the cell by the migration of ions through the salt bridge. It may be noted that the direction of current is opposite to the direction of electron flow.

redox couples are represented as Zn^{2+}/Zn and Cu^{2+}/Cu. In both cases, oxidised form is put before the reduced form. Now we put the beaker containing copper sulphate solution and the beaker containing zinc sulphate solution side by side (Fig. 8.3). We connect solutions in two beakers by a salt bridge (a U-tube containing a solution of potassium chloride or ammonium nitrate usually solidified by boiling with agar agar and later cooling to a jelly like substance). This provides an electric contact between the two solutions without allowing them to mix with each other. The zinc and copper rods are connected by a metallic wire with a provision for an ammeter and a switch. The set-up as shown in Fig.8.3 is known as Daniell cell. When the switch is in the off position, no reaction takes place in either of the beakers and no current flows through the

metallic wire. As soon as the switch is in the on position, we make the following observations:

1. The transfer of electrons now does not take place directly from Zn to Cu^{2+} but through the metallic wire connecting the two rods as is apparent from the arrow which indicates the flow of current.

2. The electricity from solution in one beaker to solution in the other beaker flows by the migration of ions through the salt bridge. We know that the flow of current is possible only if there is a potential difference between the copper and zinc rods known as **electrodes** here.

The potential associated with each electrode is known as **electrode potential**. If the concentration of each species taking part in the electrode reaction is unity (if any gas appears in the electrode reaction, it is confined to 1 atmospheric pressure) and further the reaction is carried out at 298K, then the potential of each electrode is said to be the **Standard Electrode Potential**. By convention, the standard electrode potential ($E^{\tilde{e}}$)of hydrogen electrode is 0.00 volts. The electrode potential value for each electrode process is a measure of the relative tendency of the active species in the process to remain in the oxidised/reduced form. A negative Ẽ means that the redox couple is a stronger reducing agent than the H^+/H_2 couple. A positive Ẽ means that the redox couple is a weaker reducing agent than the H^+/H_2 couple. The standard electrode potentials are very important and we can get a lot of other usefulinformation from them. The values of standard electrode potentials for some selected electrode processes (reduction reactions) are given in Table 8.1. You will learn more about electrode reactions and cells in Class XII.

Table 8.1 The Standard Electrode Potentials at 298 K

Ions are present as aqueous species and H_2O as liquid; gases and solids are shown by g and s respectively.

Reaction (Oxidised form + ne^- → Reduced form)		$E^\ominus$ / V
$F_2(g) + 2e^-$	$\rightarrow 2F^-$	2.87
$Co^{3+} + e^-$	$\rightarrow Co^{2+}$	1.81
$H_2O_2 + 2H^+ + 2e^-$	$\rightarrow 2H_2O$	1.78
$MnO_4^- + 8H^+ + 5e^-$	$\rightarrow Mn^{2+} + 4H_2O$	1.51
$Au^{3+} + 3e^-$	$\rightarrow Au(s)$	1.40
$Cl_2(g) + 2e^-$	$\rightarrow 2Cl^-$	1.36
$Cr_2O_7^{2-} + 14H^+ + 6e^-$	$\rightarrow 2Cr^{3+} + 7H_2O$	1.33
$O_2(g) + 4H^+ + 4e^-$	$\rightarrow 2H_2O$	1.23
$MnO_2(s) + 4H^+ + 2e^-$	$\rightarrow Mn^{2+} + 2H_2O$	1.23
$Br_2 + 2e^-$	$\rightarrow 2Br^-$	1.09
$NO_3^- + 4H^+ + 3e^-$	$\rightarrow NO(g) + 2H_2O$	0.97
$2Hg^{2+} + 2e^-$	$\rightarrow Hg_2^{2+}$	0.92
$Ag^+ + e^-$	$\rightarrow Ag(s)$	0.80
$Fe^{3+} + e^-$	$\rightarrow Fe^{2+}$	0.77
$O_2(g) + 2H^+ + 2e^-$	$\rightarrow H_2O_2$	0.68
$I_2(s) + 2e^-$	$\rightarrow 2I^-$	0.54
$Cu^+ + e^-$	$\rightarrow Cu(s)$	0.52
$Cu^{2+} + 2e^-$	$\rightarrow Cu(s)$	0.34
$AgCl(s) + e^-$	$\rightarrow Ag(s) + Cl^-$	0.22
$AgBr(s) + e^-$	$\rightarrow Ag(s) + Br^-$	0.10
$2H^+ + 2e^-$	**$\rightarrow H_2(g)$**	**0.00**
$Pb^{2+} + 2e^-$	$\rightarrow Pb(s)$	−0.13
$Sn^{2+} + 2e^-$	$\rightarrow Sn(s)$	−0.14
$Ni^{2+} + 2e^-$	$\rightarrow Ni(s)$	−0.25
$Fe^{2+} + 2e^-$	$\rightarrow Fe(s)$	−0.44
$Cr^{3+} + 3e^-$	$\rightarrow Cr(s)$	−0.74
$Zn^{2+} + 2e^-$	$\rightarrow Zn(s)$	−0.76
$2H_2O + 2e^-$	$\rightarrow H_2(g) + 2OH^-$	−0.83
$Al^{3+} + 3e^-$	$\rightarrow Al(s)$	−1.66
$Mg^{2+} + 2e^-$	$\rightarrow Mg(s)$	−2.36
$Na^+ + e^-$	$\rightarrow Na(s)$	−2.71
$Ca^{2+} + 2e^-$	$\rightarrow Ca(s)$	−2.87
$K^+ + e^-$	$\rightarrow K(s)$	−2.93
$Li^+ + e^-$	$\rightarrow Li(s)$	−3.05

Increasing strength of oxidising agent ↑

Increasing strength of reducing agent ↓

1. A negative $\bar{E}^\ominus$ means that the redox couple is a stronger reducing agent than the H^+/H_2 couple.

2. A positive $\bar{E}^\ominus$ means that the redox couple is a weaker reducing agent than the H^+/H_2 couple.

SUMMARY

Redox reactions form an important class of reactions in which

oxidation and reduction occur simultaneously. Three tier conceptualisation viz, classical, electronic and oxidation number, which is usually available in the texts, has been presented in detail. Oxidation, reduction, oxidising agent (oxidant) and reducing agent (reductant) have been viewed according to each conceptualisation. Oxidation numbers are assigned in accordance with a consistent set of rules. Oxidation number and ion-electron method both are useful means in writing equations for the redox reactions. Redox reactions are classified into four categories: combination, decomposition displacement and disproportionation reactions. The concept of redox couple and electrode processes is introduced here. The redox reactions find wide applications in the study of electrode processes and cells.

EXERCISES

8.1 Assign oxidation number to the underlined elements in each of the following species:

(a) $NaH_2\underline{P}O_4$ (b) $NaH\underline{S}O_4$ (c) $H_4\underline{P}_2O_7$ (d) $K_2\underline{Mn}O_4$

(e) $Ca\underline{O}_2$ (f) $Na\underline{B}H_4$ (g) $H_2\underline{S}_2O_7$ (h) $KAl(\underline{S}O_4)_2.12\ H_2O$

8.2 What are the oxidation number of the underlined elements in each of the following and how do you rationalise your results ?

(a) $K\underline{I}_3$ (b) $H_2\underline{S}_4O_6$ (c) $\underline{Fe}_3O_4$ (d) $\underline{C}H_3\underline{C}H_2OH$ (e) $\underline{C}H_3\underline{C}OOH$

8.3 Justify that the following reactions are redox reactions:

(a) $CuO(s) + H_2(g) \rightarrow Cu(s) + H_2O(g)$

(b) $Fe_2O_3(s) + 3CO(g) \rightarrow 2Fe(s) + 3CO_2(g)$

(c) $4BCl_3(g) + 3LiAlH_4(s) \rightarrow 2B_2H_6(g) + 3LiCl(s) + 3\ AlCl_3\ (s)$

(d) $2K(s) + F_2(g) \rightarrow 2K^+F^-\ (s)$

(e) $4\ NH_3(g) + 5\ O_2(g) \rightarrow 4NO(g) + 6H_2O(g)$

8.4 Fluorine reacts with ice and results in the change:

$H_2O(s) + F_2(g) \rightarrow HF(g) + HOF(g)$

Justify that this reaction is a redox reaction.

8.5 Calculate the oxidation number of sulphur, chromium and nitrogen in H_2SO_5, $Cr_2O_7^{2-}$ and NO_3^-. Suggest structure of these compounds. Count for the fallacy.

8.6 Write formulas for the following compounds:

(a) Mercury(II) chloride (b) Nickel(II) sulphate

(c) Tin(IV) oxide (d) Thallium(I) sulphate

(e) Iron(III) sulphate (f) Chromium(III) oxide

8.7 Suggest a list of the substances where carbon can exhibit oxidation states from –4 to +4 and nitrogen from –3 to +5.

8.8 While sulphur dioxide and hydrogen peroxide can act as oxidising as well as reducing agents in their reactions, ozone and nitric acid act only as oxidants. Why ?

8.9 Consider the reactions:

(a) $6\ CO_2(g) + 6H_2O(l) \rightarrow C_6H_{12}O_6(aq) + 6O_2(g)$

(b) $O_3(g) + H_2O_2(l) \rightarrow H_2O(l) + 2O_2(g)$

Why it is more appropriate to write these reactions as :

(a) $6CO_2(g) + 12H_2O(l) \rightarrow C_6H_{12}O_6(aq) + 6H_2O(l) + 6O_2(g)$

(b) $O_3(g) + H_2O_2\ (l) \rightarrow H_2O(l) + O_2(g) + O_2(g)$

Also suggest a technique to investigate the path of the above (a) and (b) redox reactions.

8.10 The compound AgF_2 is unstable compound. However, if formed, the compound acts as a very strong oxidising agent. Why ?

8.11 Whenever a reaction between an oxidising agent and a reducing

agent is carried out, a compound of lower oxidation state is formed if the reducing agent is in excess and a compound of higher oxidation state is formed if the oxidising agent is in excess. Justify this statement giving three illustrations.

8.12 How do you count for the following observations ?

(a) Though alkaline potassium permanganate and acidic potassium permanganate both are used as oxidants, yet in the manufacture of benzoic acid from toluene we use alcoholic potassium permanganate as an oxidant. Why ? Write a balanced redox equation for the reaction.

(b) When concentrated sulphuric acid is added to an inorganic mixture containing chloride, we get colourless pungent smelling gas HCl, but if the mixture contains bromide then we get red vapour of bromine. Why ?

8.13 Identify the substance oxidised reduced, oxidising agent and reducing agent for each of the following reactions:

(a) $2AgBr\ (s) + C_6H_6O_2(aq) \rightarrow 2Ag(s) + 2HBr\ (aq) + C_6H_4O_2(aq)$

(b) $HCHO(l) + 2[Ag\ (NH_3)_2]^+(aq) + 3OH^-(aq) \rightarrow 2Ag(s) + HCOO^-(aq) + 4NH_3(aq) + 2H_2O(l)$

(c) $HCHO\ (l) + 2\ Cu^{2+}(aq) + 5\ OH^-(aq) \rightarrow Cu_2O(s) + HCOO^-(aq) + 3H_2O(l)$

(d) $N_2H_4(l) + 2H_2O_2(l) \rightarrow N_2(g) + 4H_2O(l)$

(e) $Pb(s) + PbO_2(s) + 2H_2SO_4(aq) \rightarrow 2PbSO_4(s) + 2H_2O(l)$

8.14 Consider the reactions :

$2\ S_2O_3^{2-}\ (aq) + I_2(s) \rightarrow S_4\ O_6^{\ 2-}(aq) + 2I^-(aq)$

$S_2O_3^{\ 2-}(aq) + 2Br_2(l) + 5\ H_2O(l) \rightarrow 2SO_4^{2-}(aq) + 4Br^-(aq) + 10H^+(aq)$

Why does the same reductant, thiosulphate react differently with iodine and bromine ?

8.15 Justify giving reactions that among halogens, fluorine is the best oxidant and among hydrohalic compounds, hydroiodic acid is the best reductant.

8.16 Why does the following reaction occur ?

XeO_6^{4-} (aq) + $2F^-$ (aq) + $6H^+$(aq) → XeO_3(g)+ F_2(g) + $3H_2O$(l)

What conclusion about the compound Na_4XeO_6 (of which XeO_6^{4-} is a part) can be drawn from the reaction.

8.17 Consider the reactions:

(a) H_3PO_2(aq) + 4 $AgNO_3$(aq) + 2 H_2O(l) → H_3PO_4(aq) + 4Ag(s) + $4HNO_3$(aq)

(b) H_3PO_2(aq) + $2CuSO_4$(aq) + 2 H_2O(l) → H_3PO_4(aq) + 2Cu(s) + H_2SO_4(aq)

(c) C_6H_5CHO(l) + $2[Ag(NH_3)_2]^+$(aq) + $3OH^-$(aq) → $C_6H_5COO^-$(aq) + 2Ag(s) + $4NH_3$ (aq) + 2 H_2O(l)

(d) C_6H_5CHO(l) + $2Cu^{2+}$(aq) + $5OH^-$(aq) → No change observed.

What inference do you draw about the behaviour of Ag^+ and Cu^{2+} from these reactions ?

8.18 Balance the following redox reactions by ion – electron method :

(a) MnO_4^- (aq) + I^- (aq) → MnO_2 (s) + I_2(s) (in basic medium)

(b) MnO_4^- (aq) + SO_2 (g) → Mn^{2+} (aq) + HSO_4^- (aq) (in acidic solution)

(c) H_2O_2 (aq) + Fe^{2+} (aq) → Fe^{3+} (aq) + H_2O (l) (in acidic solution)

(d) $Cr_2O_7^{2-}$ + SO_2(g) → Cr^{3+} (aq) + SO_4^{2-} (aq) (in acidic solution)

8.19 Balance the following equations in basic medium by ion-electron method and oxidation number methods and identify the oxidising

agent and the reducing agent.

(a) $P_4(s) + OH^-(aq) \rightarrow PH_3(g) + HPO_2^-(aq)$

(b) $N_2H_4(l) + ClO_3^-(aq) \rightarrow NO(g) + Cl^-(g)$

(c) $Cl_2O_7(g) + H_2O_2(aq) \rightarrow ClO_2^-(aq) + O_2(g) + H^+$

8.20 What sorts of informations can you draw from the following reaction ?

$(CN)_2(g) + 2OH^-(aq) \rightarrow CN^-(aq) + CNO^-(aq) + H_2O(l)$

8.21 The Mn^{3+} ion is unstable in solution and undergoes disproportionation to give Mn^{2+}, MnO_2, and H^+ ion. Write a balanced ionic equation for the reaction.

8.22 Consider the elements :

Cs, Ne, I and F

(a) Identify the element that exhibits only negative oxidation state.

(b) Identify the element that exhibits only postive oxidation state.

(c) Identify the element that exhibits both positive and negative oxidation states.

(d) Identify the element which exhibits neither the negative nor does the positive oxidation state.

8.23 Chlorine is used to purify drinking water. Excess of chlorine is harmful. The excess of chlorine is removed by treating with sulphur dioxide. Present a balanced equation for this redox change taking place in water.

8.24 Refer to the periodic table given in your book and now answer the following questions:

(a) Select the possible non metals that can show disproportionation reaction.

(b) Select three metals that can show disproportionation reaction.

8.25 In Ostwald's process for the manufacture of nitric acid, the first step involves the oxidation of ammonia gas by oxygen gas to give nitric oxide gas and steam. What is the maximum weight of nitric oxide that can be obtained starting only with 10.00 g. of ammonia and 20.00 g of oxygen ?

8.26 Using the standard electrode potentials given in the Table 8.1, predict if the reaction between the following is feasible:

(a) $Fe^{3+}(aq)$ and $I^{-}(aq)$

(b) $Ag^{+}(aq)$ and Cu(s)

(c) Fe^{3+} (aq) and Cu(s)

(d) Ag(s) and $Fe^{3+}(aq)$

(e) $Br_2(aq)$ and $Fe^{2+}(aq)$.

8.27 Predict the products of electrolysis in each of the following:

(i) An aqueous solution of $AgNO_3$ with silver electrodes

(ii) An aqueous solution $AgNO_3$ with platinum electrodes

(iii) A dilute solution of H_2SO_4 with platinum electrodes

(iv) An aqueous solution of $CuCl_2$ with platinum electrodes.

8.28 Arrange the following metals in the order in which they displace each other from the solution of their salts.

Al, Cu, Fe, Mg and Zn.

8.29 Given the standard electrode potentials,

$K^{+}/K = -2.93V$, $Ag^{+}/Ag = 0.80V$,

$Hg^{2+}/Hg = 0.79V$

$Mg^{2+}/Mg = -2.37V$. $Cr^{3+}/Cr = -0.74V$

arrange these metals in their increasing order of reducing power.

8.30 Depict the galvanic cell in which the reaction $Zn(s) + 2Ag^{+}(aq)$

$\rightarrow Zn^{2+}(aq) + 2Ag(s)$ takes place, Further show:

(i) which of the electrode is negatively charged,

(ii) the carriers of the current in the cell, and

(iii) individual reaction at each electrode.

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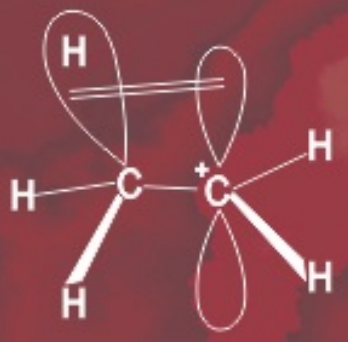
Textbook for Class XI



Unit 9
Hydrogen

Chemistry

Part II



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UNIT 9

Hydrogen

Objectives

After studying this unit, you will be able to

• present informed opinions on the position of hydrogen in the periodic table;

• identify the modes of occurrence and preparation of dihydrogen on a small and commercial scale; describe isotopes of hydrogen;

• explain how different elements combine with hydrogen to form ionic, molecular and non-stoichiometric compounds;

• describe how an understanding of its properties can lead to the production of useful substances, and new technologies;

• understand the structure of water and use the knowledge for explaining physical and chemical properties;

• explain how environmental water quality depends on a variety of dissolved substances; difference between ‘hard’ and ‘soft’ water and

learn about water softening;

• acquire the knowledge about heavy water and its importance;

• understand the structure of hydrogen peroxide, learn its preparatory methods and properties leading to the manufacture of useful chemicals and cleaning of environment;

• understand and use certain terms e.g., electron-deficient, electron-precise, electron-rich, hydrogen economy, hydrogenation etc.

*"**Hydrogen, the most abundant element in the universe and the third most abundant on the surface of the globe, is being visualised as the major future source of energy.**"*

Hydrogen has the simplest atomic structure among all the elements around us in Nature. In atomic form it consists of only one proton and one electron. However, in elemental form it exists as a diatomic (H_2) molecule and is called dihydrogen. It forms more compounds than any other element. Do you know that the global concern related to energy can be overcome to a great extent by the use of hydrogen as a source of energy? In fact, hydrogen is of great industrial importance as you will learn in this unit.

9.1 POSITION OF HYDROGEN IN THE PERIODIC TABLE

Hydrogen is the first element in the periodic table. However, its placement in the periodic table has been a subject of discussion in the past. As you know by now that the elements in the periodic table are arranged according to their electronic configurations.

Hydrogen has electronic configuration $1s^1$. On one hand, its electronic configuration is similar to the outer electronic configuration (ns^1) of alkali metals , which belong to the first group of the periodic table. On the other hand, like halogens (with ns^2np^5 configuration belonging to the seventeenth group of the periodic table), it is short by one electron to the corresponding noble gas configuration, helium ($1s^2$). Hydrogen, therefore, has resemblance to alkali metals, which lose one electron to form unipositive ions, as well as with halogens, which gain one electron to form uninegative ion. Like alkali metals, hydrogen forms oxides, halides and sulphides. However, unlike alkali metals, it has a very high ionization enthalpy and does not possess metallic characteristics under normal conditions. In fact, in terms of ionization enthalpy, hydrogen resembles more
with halogens, Δ_i H of Li is 520 kJ mol^{-1}, F is 1680 kJ mol^{-1} and that of H is 1312 kJ mol^{-1}. Like halogens, it forms a diatomic molecule, combines with elements to form hydrides and a large number of covalent compounds. However, in terms of reactivity, it is very low as compared to halogens.

Inspite of the fact that hydrogen, to a certain extent resembles both with alkali metals and halogens, it differs from them as well. Now the pertinent question arises as where should it be placed in the periodic table? Loss of the electron from hydrogen atom results in nucleus (H+) of ~1.5×10^{-3} pm size. This is extremely small as compared to normal atomic and ionic sizes of 50 to 200pm. As a consequence, H+ does not exist freely and is always associated with other atoms or molecules. Thus, it is unique in behaviour and is, therefore, best placed separately in the periodic table (Unit 3).

9.2 DIHYDROGEN, H2

9.2.1 Occurrence

Dihydrogen is the most abundant element in the universe (70% of the total mass of the universe) and is the principal element in the solar atmosphere. The giant planets Jupiter and Saturn consist mostly of hydrogen. However, due to its light nature, it is much less abundant (0.15% by mass) in the earth's atmosphere. Of course, in the combined form it constitutes 15.4% of the earth's crust and the oceans. In the combined form besides in water, it occurs in plant and animal tissues, carbohydrates, proteins, hydrides including hydrocarbons and many other compounds.

9.2.2 Isotopes of Hydrogen

Hydrogen has three isotopes: **protium**, $_1{}^1H$, deuterium, $^2{}_1H$ or D and **tritium**,$^3{}_1H$ or T. Can you guess how these isotopes differ from each other ? These isotopes differ from one another in respect of the presence of neutrons. Ordinary hydrogen, protium, has no neutrons, deuterium (also known as heavy hydrogen) has one and tritium has two neutrons in the nucleus. In the year 1934, an American scientist, Harold C. Urey, got Nobel Prize for separating hydrogen isotope of mass number 2 by physical methods.

Table 9.1 Atomic and Physical Properties of Hydrogen

Property	Hydrogen	Deuterium	Tritium
Relative abundance (%)	99.985	0.0156	10^{-15}
Relative atomic mass (g mol^{-1})	1.008	2.014	3.016
Melting point / K	13.96	18.73	20.62
Boiling point/ K	20.39	23.67	25.0
Density / gL^{-1}	0.09	0.18	0.27
Enthalpy of fusion/kJ mol^{-1}	0.117	0.197	-
Enthalpy of vaporization/kJ mol^{-1}	0.904	1.226	-
Enthalpy of bond dissociation/kJ mol^{-1} at 298.2K	435.88	443.35	-
Internuclear distance/pm	74.14	74.14	-
Ionization enthalpy/kJ mol^{-1}	1312	-	-
Electron gain enthalpy/kJ mol^{-1}	–73	-	-
Covalent radius/pm	37	-	-
Ionic radius(H^-)/pm	208		

The predominant form is protium. Terrestrial hydrogen contains 0.0156% of deuterium mostly in the form of HD. The tritium concentration is about one atom per 1018 atoms of protium. Of these isotopes, only tritium is radioactive and emits low energy

β– particles (t½, 12.33 years).

Since the isotopes have the same electronic configuration, they have almost the same chemical properties. The only difference is in their rates of reactions, mainly due to their different enthalpy of bond dissociation (Table 9.1). However, in physical properties these isotopes differ considerably due to their large mass differences.

9.3 PREPARATION OF DIHYDROGEN, H2

There are a number of methods for preparing dihydrogen from metals and metal hydrides.

9.3.1 Laboratory Preparation of Dihydrogen

(i) It is usually prepared by the reaction of granulated zinc with dilute

hydrochloric acid.

$$Zn + 2H^+ \rightarrow Zn^{2+} + H_2$$

(ii) It can also be prepared by the reaction of zinc with aqueous alkali.

$$Zn + 2NaOH \rightarrow Na_2ZnO_2 + H_2$$

Sodium zincate

9.3.2 Commercial Production of Dihydrogen

The commonly used processes are outlined below:

(i) Electrolysis of acidified water using platinum electrodes gives hydrogen.

$$2H_2O(l) \xrightarrow[\text{Traces of acid/base}]{\text{Electrolysis}} 2H_2(g) + O_2(g)$$

(ii) High purity (>99.95%) dihydrogen is obtained by electrolysing warm aqueous barium hydroxide solution between nickel electrodes.

(iii) It is obtained as a byproduct in the manufacture of sodium hydroxide and chlorine by the electrolysis of brine solution. During electrolysis, the reactions that take place are:

at anode: $2Cl^-(aq) \rightarrow Cl_2(g) + 2e^-$

at cathode: $2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$

The overall reaction is

$2Na^+(aq) + 2Cl^-(aq) + 2H_2O(l)$

$\downarrow$

$Cl_2(g) + H_2(g) + 2Na^+(aq) + 2OH^-(aq)$

(iv) Reaction of steam on hydrocarbons or coke at high temperatures in

the presence of catalyst yields hydrogen.

$$C_nH_{2n+2} + nH_2O \xrightarrow[Ni]{1270K} nCO + (2n+1)H_2$$

e.g.,

$$CH_4(g) + H_2O(g) \xrightarrow[Ni]{1270K} CO(g) + 3H_2(g)$$

The mixture of co and H_2 is called water gas. As this mixture of CO and H_2 is used for the synthesis of methanol and a number of hydrocarbons, it is also called synthesis gas or 'syngas'. Nowadays 'syngas' is produced from sewage, saw-dust, scrap wood, newspapers etc. The process of producing 'syngas' from coal is called 'coal gasification'.

$$C(s) + H_2O(g) \xrightarrow{1270K} CO(g) + H_2(g)$$

The production of dihydrogen can be increased by reacting carbon monoxide of syngas mixtures with steam in the presence of iron chromate as catalyst.

$$CO(g) + H_2O(g) \xrightarrow[catalyst]{673K} CO_2(g) + H_2(g)$$

This is called water-gas shift reaction. Carbon dioxide is removed by scrubbing with sodium arsenite solution.

Presently ~77% of the industrial dihydrogen is produced from petro-chemicals, 18% from coal, 4% from electrolysis of aqueous solutions and 1% from other sources.

9.4 PROPERTIES OF DIHYDROGEN

9.4.1 Physical Properties

Dihydrogen is a colourless, odourless, tasteless, combustible gas. It is lighter than air and insoluble in water. Its other physical properties

alongwith those of deuterium are given in Table 9.1.

9.4.2 Chemical Properties

The chemical behaviour of dihydrogen (and for that matter any molecule) is determined, to a large extent, by bond dissociation enthalpy. The H–H bond dissociation enthalpy is the highest for a single bond between two atoms of any element. What inferences would you draw from this fact ? It is because of this factor that the dissociation of dihydrogen into its atoms is only ~0.081% around 2000K which increases to 95.5% at 5000K. Also, it is relatively inert at room temperature due to the high H–H bond enthalpy. Thus, the atomic hydrogen is produced at a high temperature in an electric arc or under ultraviolet radiations. Since its orbital is incomplete with 1s1 electronic configuration, it does combine with almost all the elements. It accomplishes reactions by (i) loss of the only electron to
give H+, (ii) gain of an electron to form H–, and (iii) sharing electrons to form a single covalent bond.

The chemistry of dihydrogen can be illustrated by the following reactions:

Reaction with halogens: It reacts with halogens, X_2 to give hydrogen halides, HX,

$$H_2(g) + X_2(g) \rightarrow 2HX(g) \quad (X = F, Cl, Br, I)$$

While the reaction with fluorine occurs even in the dark, with iodine it requires a catalyst.

Reaction with dioxygen: It reacts with dioxygen to form water. The reaction is highly exothermic.

$$2H_2(g) + O_2(g) \xrightarrow{\text{catalyst or heating}} 2H_2O(l);$$

$\Delta H^{\ominus}$ = –285.9 kJ mol–1

Reaction with dinitrogen: With dinitrogen it forms ammonia.

$$3H_2(g) + N_2(g) \xrightarrow[Fe]{673K,200atm} 2NH_3(g);$$
$$\Delta H^{\ominus} = -92.6 \text{ kJ mol}^{-1}$$

This is the method for the manufacture of ammonia by the Haber process.

Reactions with metals: With many metals it combines at a high temperature to yield the corresponding hydrides (section 9.5)

$H_2(g) + 2M(g) \rightarrow 2MH(s)$;

where M is an alkali metal

Reactions with metal ions and metal oxides: It reduces some metal ions in aqueous solution and oxides of metals (less active than iron) into corresponding metals.

$$H_2(g) + Pd^{2+}(aq) \rightarrow Pd(s) + 2H^+(aq)$$
$$yH_2(g) + M_xO_y(s) \rightarrow xM(s) + yH_2O(l)$$

Reactions with organic compounds: It reacts with many organic compounds in the presence of catalysts to give useful hydrogenated products of commercial importance. For example :

(i) Hydrogenation of vegetable oils using nickel as catalyst gives edible fats (margarine and vanaspati ghee)

(ii) Hydroformylation of olefins yields aldehydes which further undergo reduction to give alcohols.

$$H_2 + CO + RCH = CH_2 \rightarrow RCH_2CH_2CHO$$

$$H_2 + RCH_2CH_2CHO \rightarrow RCH_2CH_2CH_2OH$$

Problem 9.1

Comment on the reactions of dihydrogen with (i) chlorine, (ii) sodium, and (iii) copper(II) oxide

Solution

(i) Dihydrogen reduces chlorine into chloride (Cl^-) ion and itself gets oxidised to H+ ion by chlorine to form hydrogen chloride. An electron pair is shared between H and Cl leading to the formation of a covalent molecule.

(ii) Dihydrogen is reduced by sodium to form NaH. An electron is transferred from Na to H leading to the formation of an ionic compound, Na^+H^-.

(iii) Dihydrogen reduces copper(II) oxide to copper in zero oxidation state and itself gets oxidised to H_2O, which is a covalent molecule.

9.4.3 Uses of Dihydrogen

• The largest single use of dihydrogen is in the synthesis of ammonia which is used in the manufacture of nitric acid and nitrogenous fertilizers.

• Dihydrogen is used in the manufacture of vanaspati fat by the hydrogenation of polyunsaturated vegetable oils like soyabean, cotton seeds etc.

• It is used in the manufacture of bulk organic chemicals, particularly methanol.

$$CO(g) + 2H_2(g) \xrightarrow[\text{catalyst}]{\text{cobalt}} CH_3OH(l)$$

• It is widely used for the manufacture of metal hydrides (Section 9.5)

• It is used for the preparation of hydrogen chloride, a highly useful

chemical.

• In metallurgical processes, it is used to reduce heavy metal oxides to metals.

• Atomic hydrogen and oxy-hydrogen torches find use for cutting and welding purposes. Atomic hydrogen atoms (produced by dissociation of dihydrogen with the help of an electric arc) are allowed to recombine on the surface to be welded to generate the temperature of 4000 K.

• It is used as a rocket fuel in space research.

• Dihydrogen is used in fuel cells for generating electrical energy. It has many advantages over the conventional fossil fuels and electric power. It does not produce any pollution and releases greater energy per unit mass of fuel in comparison to gasoline and other fuels.

9.5 HYDRIDES

Dihydrogen, under certain reaction conditions, combines with almost all elements, except noble gases, to form binary compounds, called hydrides. If 'E' is the symbol of an element then hydride can be expressed as EHx (e.g., MgH_2) or EmHn (e.g., B_2H_6).

The hydrides are classified into three categories :

(i) Ionic or saline or saltlike hydrides

(ii) Covalent or molecular hydrides

(iii) Metallic or non-stoichiometric hydrides

9.5.1 Ionic or Saline Hydrides

These are stoichiometric compounds of dihydrogen formed with most of

the s-block elements which are highly electropositive in character. However, significant covalent character is found in the lighter metal hydrides such as LiH, BeH2 and MgH_2. In fact BeH_2 and MgH_2 are polymeric in structure. The ionic hydrides are crystalline, non-volatile and non-conducting in solid state. However, their melts conduct electricity and on electrolysis liberate dihydrogen gas at anode, which confirms the existence of H^- ion.

$$2H^-(\text{melt}) \xrightarrow{\text{ancde}} H_2(g) + 2e^-$$

Saline hydrides react violently with water producing dihydrogen gas.

$$NaH(s) + H_2O(aq) \rightarrow NaOH(aq) + H_2(g)$$

Lithium hydride is rather unreactive at moderate temperatures with O_2 or Cl_2. It is, therefore, used in the synthesis of other useful hydrides, e.g.,

$$8LiH + Al_2Cl_6 \rightarrow 2LiAlH_4 + 6LiCl$$

$$2LiH + B_2H_6 \rightarrow 2LiBH_4$$

9.5.2 Covalent or Molecular Hydride

Dihydrogen forms molecular compounds with most of the p-block elements. Most familiar examples are CH_4, NH_3, H_2O and HF. For convenience hydrogen compounds of non-metals have also been considered as hydrides. Being covalent, they are volatile compounds.

Molecular hydrides are further classified according to the relative numbers of electrons and bonds in their Lewis structure into :

(i) electron-deficient, (ii) electron-precise, and (iii) electron-rich hydrides.

An electron-deficient hydride, as the name suggests, has too few electrons for writing its conventional Lewis structure. Diborane (B_2H_6) is an example. In fact all elements of group 13 will form electron-deficient compounds. What do you expect from their behaviour? They act as Lewis acids i.e., electron acceptors.

Electron-precise compounds have the required number of electrons to write their conventional Lewis structures. All elements of group 14 form such compounds (e.g., CH_4) which are tetrahedral in geometry.

Electron-rich hydrides have excess electrons which are present as lone pairs. Elements of group 15-17 form such compounds. (NH3 has 1- lone pair, H_2O – 2 and HF –3 lone pairs). What do you expect from the behaviour of such compounds ? They will behave as Lewis bases i.e., electron donors. The presence of lone pairs on highly electronegative atoms like N, O and F in hydrides results in hydrogen bond formation between the molecules. This leads to the association of molecules.

Problem 9.2

Would you expect the hydrides of N, O and F to have lower boiling points than the hydrides of their subsequent group members ? Give reasons.

Solution

On the basis of molecular masses of NH_3, H_2O and HF, their boiling points are expected to be lower than those of the subsequent group member hydrides. However, due to higher electronegativity of N, O and F, the magnitude of hydrogen bonding in their hydrides will be quite appreciable. Hence, the boiling points NH_3, H_2O and HF will be higher than the hydrides of their subsequent group members.

9.5.3 Metallic or Non-stoichiometric (or Interstitial) Hydrides

These are formed by many d-block and f-block elements. However, the metals of group 7, 8 and 9 do not form hydride. Even from group 6, only chromium forms CrH. These hydrides conduct heat and electricity though not as efficiently as their parent metals do. Unlike saline hydrides, they are almost always non-stoichiometric, being deficient in hydrogen. For example, $LaH_{2.87}$, $YbH_{2.55}$, $TiH_{1.5–1.8}$, $ZrH_{1.3–1.75}$, $VH_{0.56}$, $NiH_{0.6–0.7}$, $PdH_{0.6–0.8}$ etc. In such hydrides, the law of constant composition does not hold good.

Earlier it was thought that in these hydrides, hydrogen occupies interstices in the metal lattice producing distortion without any change in its type. Consequently, they were termed as interstitial hydrides. However, recent studies have shown that except for hydrides of Ni, Pd, Ce and Ac, other hydrides of this class have lattice different from that of the parent metal. The property of absorption of hydrogen on transition metals is widely used in catalytic reduction / hydrogenation reactions for the preparation of large number of compounds. Some of the metals (e.g., Pd, Pt) can accommodate a very large volume of hydrogen and, therefore, can be used as its storage media. This property has high potential for **hydrogen storage** and as a **source of energy**.

Problem 9.3

Can phosphorus with outer electronic configuration $3s^2 3p^3$ form PH_5 ?

Solution

Although phosphorus exhibits +3 and +5 oxidation states, it cannot

form PH_5. Besides some other considerations, high ΔaH value of dihydrogen and ΔegH value of hydrogen do not favour to exhibit the highest oxidation state of P, and consequently the formation of PH_5.

9.6 WATER

A major part of all living organisms is made up of water. Human body has about 65% and some plants have as much as 95% water. It is a crucial compound for the survival of all life forms. It is a solvent of great importance. The distribution of water over the earth's surface is not uniform. The estimated world water supply is given in Table 9.2

Table 9.2 Estimated World Water Supply

Source	% of Total
Oceans	97.33
Saline lakes and inland seas	0.008
Polar ice and glaciers	2.04
Ground water	0.61
Lakes	0.009
Soil moisture	0.005
Atmospheric water vapour	0.001
Rivers	0.0001

9.6.1 Physical Properties of Water

It is a colourless and tasteless liquid. Its physical properties are given in Table 9.3 along with the physical properties of heavy water.

The unusual properties of water in the condensed phase (liquid and solid states) are due to the presence of extensive hydrogen bonding between water molecules. This leads to high freezing point, high boiling point, high

heat of vaporisation and high heat of fusion in comparison to H_2S and H_2Se. In comparison to other liquids, water has a higher specific heat, thermal conductivity, surface tension, dipole moment and dielectric constant, etc. These properties allow water to play a key role in the biosphere.

The high heat of vaporisation and heat capacity are responsible for moderation of the climate and body temperature of living beings. It is an excellent solvent for transportation of ions and molecules required for plant and animal metabolism. Due to hydrogen bonding with polar molecules, even covalent compounds like alcohol and carbohydrates dissolve in water.

Table 9.3 Physical Properties of H_2O and D_2O

Property	H_2O	D_2O
Molecular mass (g mol^{-1})	18.0151	20.0276
Melting point/K	273.0	276.8
Boiling point/K	373.0	374.4
Enthalpy of formation/kJ mol^{-1}	–285.9	–294.6
Enthalpy of vaporisation (373K)/kJ mol^{-1}	40.66	41.61
Enthalpy of fusion/kJ mol^{-1}	6.01	-
Temp of max. density/K	276.98	284.2
Density (298K)/g cm^{-3}	1.0000	1.1059
Viscosity/centipoise	0.8903	1.107
Dielectric constant/$C^2/N.m^2$	78.39	78.06
Electrical conductivity (293K/ohm^{-1} cm^{-1})	5.7×10^{-8}	-

9.6.2 Structure of Water

In the gas phase water is a bent molecule with a bond angle of 104.5°, and O–H bond length of 95.7 pm as shown in Fig 9.1(a). It is a highly polar molecule, (Fig 9.1(b)). Its orbital overlap picture is shown in Fig. 9.1(c). In the liquid phase water molecules are associated together by hydrogen bonds.

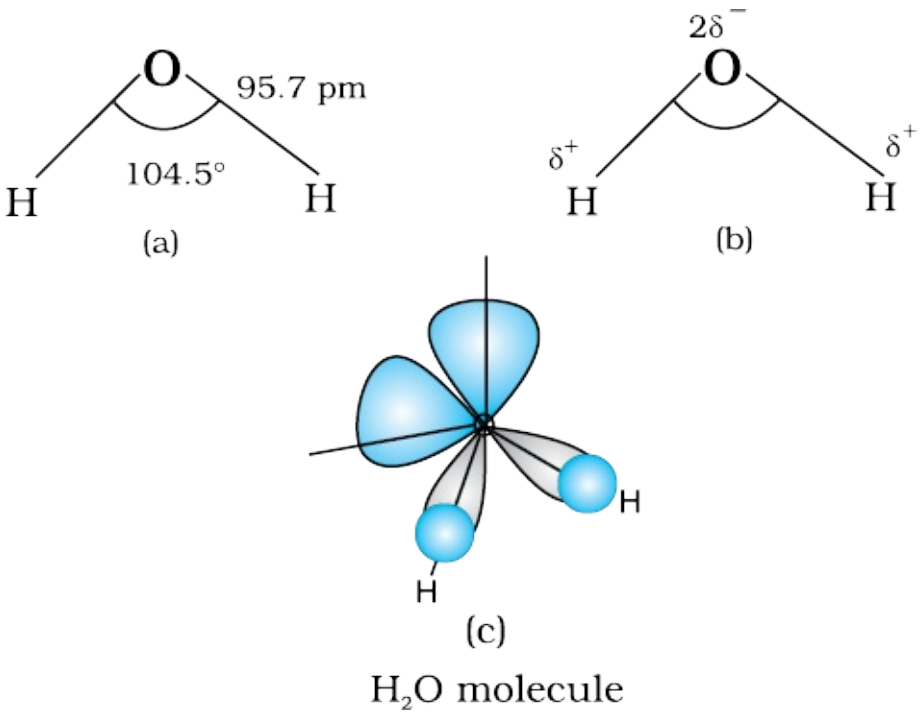


Fig. 9.1 (a) The bent structure of water; (b) the water molecule as a dipole and (c) the orbital overlap picture in water molecule.

The crystalline form of water is ice. At atmospheric pressure ice crystallises in the hexagonal form, but at very low temperatures it condenses to cubic form. Density of ice is less than that of water. Therefore, an ice cube floats on water. In winter season ice formed on the surface of a lake provides thermal insulation which ensures the survival of the aquatic life. This fact is of great ecological significance.

9.6.3 Structure of Ice

Ice has a highly ordered three dimensional hydrogen bonded structure as shown in Fig. 9.2. Examination of ice crystals with X-rays shows that each oxygen atom is surrounded tetrahedrally by four other oxygen atoms at a distance of 276 pm.

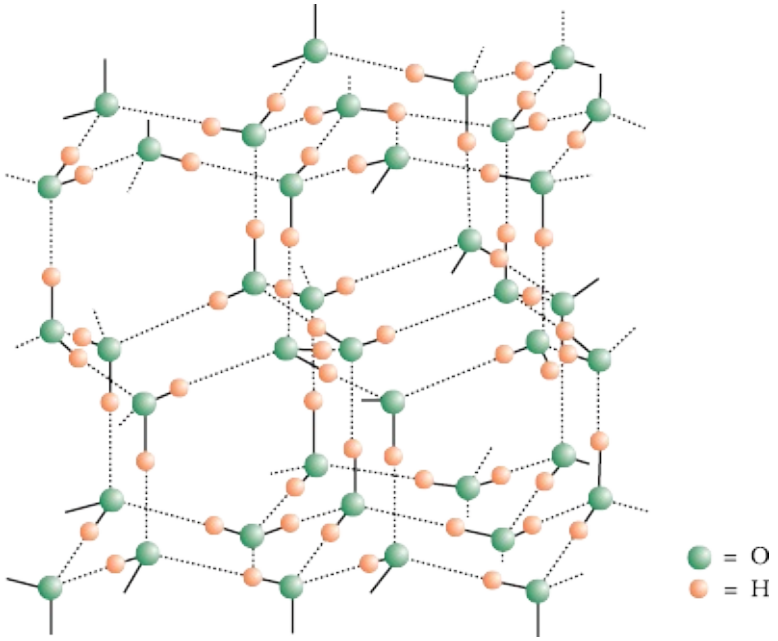


Fig. 9.2 The structure of ice

Hydrogen bonding gives ice a rather open type structure with wide holes. These holes can hold some other molecules of appropriate size interstitially.

9.6.4 Chemical Properties of Water

Water reacts with a large number of substances. Some of the important reactions are given below.

(1) Amphoteric Nature: It has the ability to act as an acid as well as a base i.e., it behaves as an amphoteric substance. In the Brönsted sense it acts as an acid with NH3 and a base with H2S.

$$H_2O(l) + NH_3(aq) \rightleftharpoons OH^-(aq) + NH_4^+(aq)$$

$$H_2O(l) + H_2S(aq) \rightleftharpoons H_3O^+(aq) + HS^-(aq)$$

The auto-protolysis (self-ionization) of water takes place as follows :

$$H_2O(l) + H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$$

acid-1 base-2 acid-2 base-1

(acid) (base) (conjugate acid) (conjugate base)

(2) Redox Reactions Involving Water: Water can be easily reduced to dihydrogen by highly electropositive metals.

$$2H_2O(l) + 2Na(s) \rightarrow 2NaOH(aq) + H_2(g)$$

Thus, it is a great source of dihydrogen.

Water is oxidised to O_2 during photosynthesis.

$$6CO_2(g) + 12H_2O(l) \rightarrow C_6H1_2O_6(aq) + 6H_2O(l) + 6O_2(g)$$

With fluorine also it is oxidised to O_2.

$$2F_2(g) + 2H_2O(l) \rightarrow 4H+ (aq) + 4F–(aq) + O_2(g)$$

(3) Hydrolysis Reaction: Due to high dielectric constant, it has a very strong hydrating tendency. It dissolves many ionic compounds. However, certain covalent and some ionic compounds are hydrolysed in water.

$$P_4O_{10}(s) + 6H_2O(l) \rightarrow 4H_3PO_4(aq)$$

$$SiCl_4(l) + 2H_2O(l) \rightarrow SiO_2(s) + 4HCl(aq)$$

$$N^{3-}(s) + 3H_2O(l) \rightarrow NH_3(g) + 3OH^-(aq)$$

(4) Hydrates Formation: From aqueous solutions many salts can be crystallised as hydrated salts. Such an association of water is of different types viz.,

(i) coordinated water e.g.,

$$\left[Cr(H_2O)_6\right]^{3+} 3Cl^-$$

(ii) interstitial water e.g.,

$$BaCl_2.2H_2O$$

(iii) hydrogen-bonded water e.g.,

$$\left[Cu(H_2O)_4\right]^{2+} SO_4^{2-}.H_2O \text{ in } CuSO_4.5H_2O.$$

Problem 9.4

How many hydrogen-bonded water molecule(s) are associated in $CuSO_4.5H_2O$?

Solution

Only one water molecule, which is outside the brackets (coordination sphere), is hydrogen-bonded. The other four molecules of water are coordinated.

9.6.5 Hard and Soft Water

Rain water is almost pure (may contain some dissolved gases from the atmosphere). Being a good solvent, when it flows on the surface of the earth, it dissolves many salts. Presence of calcium and magnesium salts in the form of hydrogencarbonate, chloride and sulphate in water makes water **'hard'. Hard water** does not give lather with soap. Water free from soluble salts of calcium and magnesium is called **Soft water**. It gives lather with soap easily.

Hard water forms scum/precipitate with soap. Soap containing sodium stearate ($C_{17}H_{35}COONa$) reacts with hard water to precipitate out Ca/Mg stearate.

$$2C_{17}H_{35}COONa(aq) + M^{2+}(aq) \rightarrow$$
$$(C_{17}H_{35}COO)_2\ M \downarrow + 2Na^{+}(aq);\ M \text{ is } Ca/Mg$$

It is, therefore, unsuitable for laundry. It is harmful for boilers as well, because of deposition of salts in the form of scale. This reduces the efficiency of the boiler. The hardness of water is of two types: (i) temporary hardness, and (ii) permanent hardness.

9.6.6 Temporary Hardness

Temporary hardness is due to the presence of magnesium and calcium hydrogen-carbonates. It can be removed by :

(i) Boiling: During boiling, the soluble $Mg(HCO_3)_2$ is converted into insoluble $Mg(OH)_2$ and $Ca(HCO_3)_2$ is changed to insoluble $CaCO_3$. It is because of high solubility product of Mg(OH)2 as compared to that of $MgCO_3$, that $Mg(OH)_2$ is precipitated. These precipitates can be removed by filtration. Filtrate thus obtained will be soft water.

$$Mg(HCO_3)_2 \xrightarrow{\text{Heating}} Mg(OH)_2 \downarrow + 2CO_2 \uparrow$$
$$Ca(HCO_3)_2 \xrightarrow{\text{Heating}} CaCO_3 \downarrow + H_2O + CO_2 \uparrow$$

(ii) Clark's method: In this method calculated amount of lime is added to hard water. It precipitates out calcium carbonate and magnesium hydroxide which can be filtered off.

$$Ca(HCO_3)_2 + Ca(OH)_2 \rightarrow 2CaCO_3 \downarrow + 2H_2O$$
$$Mg(HCO_3)_2 + 2Ca(OH)_2 \rightarrow 2CaCO_3 \downarrow + Mg(OH)_2 \downarrow + 2H_2O$$

9.6.7 Permanent Hardness

It is due to the presence of soluble salts of magnesium and calcium in the form of chlorides and sulphates in water. Permanent hardness is not removed by boiling. It can be removed by the following methods:

(i) Treatment with washing soda (sodium carbonate): Washing soda reacts with soluble calcium and magnesium chlorides and sulphates in hard water to form insoluble carbonates.

$$MCl_2 + Na_2CO_3 \rightarrow MCO_3 \downarrow + \ 2NaCl \quad (M = Mg, Ca)$$

$$MSO_4 + Na_2CO_3 \rightarrow \ MCO_3 \downarrow + \ Na_2SO_4$$

(ii) Calgon's method: Sodium hexameta-phosphate ($Na_6P_6O_{18}$), commercially called 'calgon', when added to hard water, the following reactions take place.

$$Na_6P_6O_{18} \rightarrow 2Na^+ + Na_4P_6O_{18}^{2-} \quad (M = Mg, Ca)$$

$$M^{2+} + Na_4P_6O_{18}^{2-} \rightarrow [Na_2MP_6O_{18}]^{2-} + 2Na^+$$

The complex anion keeps the Mg^{2+} and Ca^{2+} ions in solution.

(iii) Ion-exchange method: This method is also called zeolite/permutit process. Hydrated sodium aluminium silicate is zeolite/permutit. For the sake of simplicity, sodium aluminium silicate ($NaAlSiO_4$) can be written as NaZ. When this is added in hard water, exchange reactions take place.

$$2NaZ(s) + M^{2+}(aq) \rightarrow MZ_2(s) + 2Na^{+}(aq)$$
$$(M = Mg, Ca)$$

Permutit/zeolite is said to be exhausted when all the sodium in it is used up. It is regenerated for further use by treating with an aqueous sodium chloride solution.

$$MZ_2(s) + 2NaCl(aq) \rightarrow 2NaZ(s) + MCl_2(aq)$$

(iv) Synthetic resins method: Nowadays hard water is softened by using synthetic cation exchangers. This method is more efficient than zeolite process. Cation exchange resins contain large organic molecule with - SO_3H group and are water insoluble. Ion exchange resin (RSO_3H) is changed to RNa by treating it with NaCl. The resin exchanges Na^+ ions with Ca^{2+} and Mg^{2+} ions present in hard water to make the water soft. Here R is resin anion.

$$2RNa(s) + M^{2+}(aq) \rightarrow R_2M(s) + 2Na^{+}(aq)$$

The resin can be regenerated by adding aqueous NaCl solution.

Pure de-mineralised (de-ionized) water free from all soluble mineral salts is obtained by passing water successively through a cation exchange (in the H^+ form) and an anion-exchange (in the OH^- form) resins:

$$2RH(s) + M^{2+}(aq) \rightleftharpoons MR_2(s) + 2H^{+}(aq)$$

In this cation exchange process, H+ exchanges for Na^+, Ca^{2+}, Mg^{2+} and other cations present in water. This process results in proton release and thus makes the water acidic. In the anion exchange process:

$$RNH_2(s) + H_2O(l) \rightleftharpoons RNH_3^{+}.OH^{-}(s)$$

$$RNH_3^+.OH^-(s) + X^-(aq) \rightleftharpoons RNH_3^+.X^-(s) + OH^-(aq)$$

OH^- exchanges for anions like Cl^-, HCO_3^-, SO_4^{2-} etc. present in water.

OH^- ions, thus, liberated neutralise the H^+ ions set free in the cation exchange.

$$H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$$

The exhausted cation and anion exchange resin beds are regenerated by treatment with dilute acid and alkali solutions respectively.

9.7 HYDROGEN PEROXIDE (H_2O_2)

Hydrogen peroxide is an important chemical used in pollution control treatment of domestic and industrial effluents.

9.7.1 Preparation

It can be prepared by the following methods.

(i) Acidifying barium peroxide and removing excess water by evaporation under reduced pressure gives hydrogen peroxide.

$$BaO_2.8H_2O(s) + H_2SO_4(aq) \rightarrow BaSO_4(s) + H_2O_2(aq) + 8H_2O(l)$$

(ii) Peroxodisulphate, obtained by electrolytic oxidation of acidified sulphate solutions at high current density, on hydrolysis yields hydrogen peroxide.

$$2HSO_4^-(aq) \xrightarrow{\text{Electrolysis}} HO_3SOOSO_3H(aq)$$
$$\xrightarrow{\text{Hydrolysis}} 2HSO_4^-(aq) + 2H^+(aq) + H_2O_2(aq)$$

This method is now used for the laboratory preparation of D2O2.

$$K_2S_2O_8(s) + 2D_2O(l) \rightarrow 2KDSO_4(aq) + D_2O_2(l)$$

(iii) Industrially it is prepared by the auto-oxidation of 2-alklylanthraquinols.

$$2-\text{ethylanthraquinol} \underset{H_2/Pd}{\overset{O_2(air)}{\rightleftharpoons}} H_2O_2 + (\text{oxidised product})$$

In this case 1% H_2O_2 is formed. It is extracted with water and concentrated to ~30% (by mass) by distillation under reduced pressure. It can be further concentrated to ~85% by careful distillation under low pressure. The remaining water can be frozen out to obtain pure H_2O_2.

9.7.2 Physical Properties

In the pure state H_2O_2 is an almost colourless (very pale blue) liquid. Its important physical properties are given in Table 9.4.

H_2O_2 is miscible with water in all proportions and forms a hydrate $H_2O_2.H_2O$ (mp 221K). A 30% solution of H_2O_2 is marketed as '100 volume' hydrogen peroxide. It means that one millilitre of 30% H_2O_2 solution will give 100 mL of oxygen at STP. Commercially marketed sample is 10 V, which means that the sample contains 3% H_2O_2.

Problem 9.5

Calculate the strength of 10 volume solution of hydrogen peroxide.

Solution

10 volume solution of H_2O_2 means that 1L of this H_2O_2 solution will give 10 L of oxygen at STP

$$2H_2O_2(l) \rightarrow O_2(g) + H_2O(l)$$

2×34 g 22.7 L at STP

68 g

On the basis of above equation 22.7 L of O2 is produced from 68 g H2O2 at STP

10 L of O_2 at STP is produced from

$$\frac{68 \times 10}{22.7} g = 29.9 \text{ g} \approx 30 \text{ g } H_2O_2$$

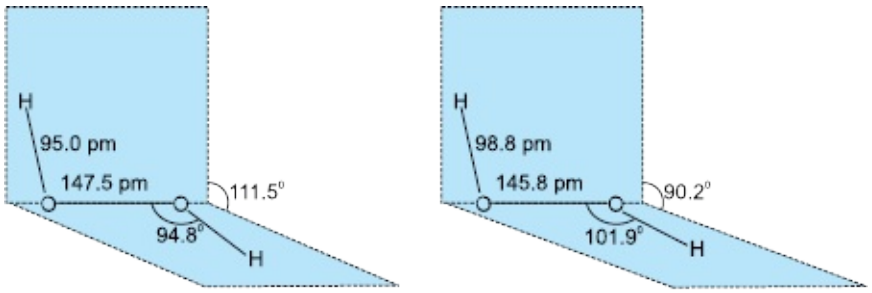
Therefore, strength of H_2O_2 in 10 volume H_2O_2 solution = 30 g/L = 3% H_2O_2 solution

Table 9.4 Physical Properties of Hydrogen Peroxide

Melting point/K	272.4	Density (liquid at 298 K)/g cm^{-3}	1.44
Boiling point(exrapolated)/K	423	Viscosity (290K)/centipoise	1.25
Vapour pressure(298K)/mmHg	1.9	Dielectric constant (298K)/$C^2/N\ m^2$	70.7
Density (solid at 268.5K)/g cm^{-3}	1.64	Electrical conductivity (298K)/$\Omega^{-1}\ cm^{-1}$	5.1×10^{-8}

9.7.3 Structure

Hydrogen peroxide has a non-planar structure. The molecular dimensions in the gas phase and solid phase are shown in Fig 9.3



(a) Gas phase (b) Solid phase

Fig. 9.3 (a) H_2O_2 structure in gas phase, dihedral angle is 111.5°. (b) H_2O_2 structure in solid phase at 110K, dihedral angle is 90.2°.

9.7.4 Chemical Properties

It acts as an oxidising as well as reducing agent in both acidic and alkaline media. Simple reactions are described below.

(i) Oxidising action in acidic medium

$$2Fe^{2+}(aq) + 2H^{+}(aq) + H_2O_2(aq) \rightarrow 2Fe^{3+}(aq) + 2H_2O(l)$$

$$PbS(s) + 4H_2O_2(aq) \rightarrow PbSO_4(s) + 4H_2O(l)$$

(ii) Reducing action in acidic medium

$$2MnO_4^- + 6H^+ + 5H_2O_2 \rightarrow 2Mn^{2+} + 8H_2O + 5O_2$$

$$HOCl + H_2O_2 \rightarrow H_3O^+ + Cl^- + O_2$$

(iii) Oxidising action in basic medium

$$2Fe^{2+} + H_2O_2 \rightarrow 2Fe^{3+} + 2OH^-$$

$$Mn^{2+} + H_2O_2 \rightarrow Mn^{4+} + 2OH^-$$

(iv) Reducing action in basic medium

$$I_2 + H_2O_2 + 2OH^- \rightarrow 2I^- + 2H_2O + O_2$$

$$2MnO_4^- + 3H_2O_2 \rightarrow 2MnO_2 + 3O_2 + 2H_2O + 2OH^-$$

9.7.5 Storage

H_2O_2 decomposes slowly on exposure to light.

$$2H_2O_2(l) \rightarrow 2H_2O(l) + O_2(g)$$

In the presence of metal surfaces or traces of alkali (present in glass containers), the above reaction is catalysed. It is, therefore, stored in wax-lined glass or plastic vessels in dark. Urea can be added as a stabiliser. It is kept away from dust because dust can induce explosive decomposition of the compound.

9.7.6 Uses

Its wide scale use has led to tremendous increase in the industrial production of H_2O_2. Some of the uses are listed below:

(i) In daily life it is used as a hair bleach and as a mild disinfectant. As an antiseptic it is sold in the market as perhydrol.

(ii) It is used to manufacture chemicals like sodium perborate and per-carbonate, which are used in high quality detergents.

(iii) It is used in the synthesis of hydroquinone, tartaric acid and certain food products and pharmaceuticals (cephalosporin) etc.

(iv) It is employed in the industries as a bleaching agent for textiles, paper pulp, leather, oils, fats, etc.

(v) Nowadays it is also used in Environmental (Green) Chemistry. For

example, in pollution control treatment of domestic and industrial effluents, oxidation of cyanides, restoration of aerobic conditions to sewage wastes, etc.

9.8 HEAVY WATER, D_2O

It is extensively used as a moderator in nuclear reactors and in exchange reactions for the study of reaction mechanisms. It can be prepared by exhaustive electrolysis of water or as a by-product in some fertilizer industries. Its physical properties are given in Table 9.3. It is used for the preparation of other deuterium compounds, for example:

$$CaC_2 + 2D_2O \rightarrow C_2D_2 + Ca(OD)_2$$
$$SO_3 + D_2O \rightarrow D_2SO_4$$
$$Al_4C_3 + 12D_2O \rightarrow 3CD_4 + 4Al(OD)_3$$

9.9 DIHYDROGEN AS A FUEL

Dihydrogen releases large quantities of heat on combustion. The data on energy released by combustion of fuels like dihydrogen, methane, LPG etc. are compared in terms of the same amounts in mole, mass and volume, are shown in Table 9.5.

From this table it is clear that on a mass for mass basis dihydrogen can release more energy than petrol (about three times). Moreover, pollutants in combustion of dihydrogen will be less than petrol. The only pollutants will be the oxides of dinitrogen (due to the presence of dinitrogen as impurity with dihydrogen). This, of course, can be minimised by injecting a small amount of water into the cylinder to lower the temperature so that the reaction between dinitrogen and dioxygen may not take place. However, the mass of the containers in which dihydrogen will be kept must be taken into consideration. A cylinder of compressed dihydrogen

weighs about 30 times as much as a tank of petrol containing the same amount of energy. Also, dihydrogen gas is converted into liquid state by cooling to 20K. This would require expensive insulated tanks. Tanks of metal alloy like $NaNi_5$, Ti–TiH_2, Mg–MgH_2 etc. are in use for storage of dihydrogen in small quantities. These limitations have prompted researchers to search for alternative techniques to use dihydrogen in an efficient way.

In this view **Hydrogen Economy** is an alternative. The basic principle of hydrogen economy is the transportation and storage of energy in the form of liquid or gaseous dihydrogen. Advantage of hydrogen economy is that energy is transmitted in the form of dihydrogen and not as electric power. It is for the first time in the history of India that a pilot project using dihydrogen as fuel was launched in October 2005 for running automobiles. Initially 5% dihydrogen has been mixed in CNG for use in four-wheeler vehicles. The percentage of dihydrogen would be gradually increased to reach the optimum level.

Nowadays, it is also used in fuel cells for generation of electric power. It is expected that economically viable and safe sources of dihydrogen will be identified in the years to come, for its usage as a common source of energy.

Table 9.5 The Energy Released by Combustion of Various Fuels in Moles, Mass and Volume

Energy released on combustion in kJ state)	Dihydrogen (in gaseous state)	Dihydrogen (in liquid)	LPG	CH_4 gas	Octane (in liquid state)
per mole	286	285	2220	880	5511
per gram	143	142	50	53	47
per litre	12	9968	25590	35	34005

Summary

Hydrogen is the lightest atom with only one electron. Loss of this electron results in an elementary particle, the proton. Thus, it is unique in character. It has three isotopes, namely : **protium** ($^{1}_{1}H$), deuterium (D or $^{2}_{1}H$) and **tritium** (T or $^{3}_{1}H$). Amongst these three, only tritium is radioactive. Inspite of its resemblance both with alkali metals and halogens, it occupies a separate position in the periodic table because of its unique properties.

Hydrogen is the most abundant element in the universe. In the free state it is almost not found in the earth's atmosphere. However, in the combined state, it is the third most abundant element on the earth's surface.

Dihydrogen on the industrial scale is prepared by the **water-gas shift** reaction from petrochemicals. It is obtained as a byproduct by the electrolysis of brine.

The H–H **bond dissociation enthalpy** of dihydrogen (435.88 kJ mol–1) is the highest for a single bond between two atoms of any elements. This property is made use of in the atomic hydrogen torch which generates a temperature of ~4000K and is ideal for welding of high melting metals.

Though dihydrogen is rather inactive at room temperature because of very high negative dissociation enthalpy, it combines with almost all the elements under appropriate conditions to form **hydrides**. All the type of hydrides can be classified into three categories: ionic or saline hydrides, covalent or molecular hydrides and metallic or non-stoichiometric hydrides. Alkali metal hydrides are good reagents for preparing other hydride compounds. Molecular hydrides (e.g., B2H6, CH4, NH3, H2O) are of great importance in day-to-day life. Metallic hydrides are useful for ultrapurification of dihydrogen and as dihydrogen storage media.

Among the other chemical reactions of dihydrogen, **reducing reactions** leading to the formation hydrogen halides, water, ammonia, methanol, vanaspati ghee, etc. are of great importance. In

metallurgical process, it is used to reduce metal oxides. In space programmes, it is used as a rocket fuel. In fact, it has promising potential for use as a non-polluting fuel of the near future (**Hydrogen Economy**).

Water is the most common and abundantly available substance. It is of a great chemical and biological significance. The ease with which water is transformed from liquid to solid and to gaseous state allows it to play a vital role in the **biosphere**. The water molecule is highly polar in nature due to its bent structure. This property leads to hydrogen bonding which is the maximum in ice and least in water vapour. The polar nature of water makes it: (a) a very good solvent for ionic and partially ionic compounds; (b) to act as an amphoteric (acid as well as base) substance; and (c) to form hydrates of different types. Its property to dissolve many salts, particularly in large quantity, makes it hard and hazardous for industrial use. Both temporary and permanent **hardness** can be removed by the use of zeolites, and synthetic ion-exchangers.

Heavy water, D_2O is another important compound which is manufactured by the electrolytic enrichment of normal water. It is essentially used as a moderator in nuclear reactors.

Hydrogen peroxide, H_2O_2 has an interesting non-polar structure and is widely used as an industrial bleach and in pharmaceutical and pollution control treatment of industrial and domestic effluents.

Exercises

9.1 Justify the position of hydrogen in the periodic table on the basis of its electronic configuration.

9.2 Write the names of isotopes of hydrogen. What is the mass ratio of these isotopes?

9.3 Why does hydrogen occur in a diatomic form rather than in a monoatomic form under normal conditions?

9.4 How can the production of dihydrogen, obtained from 'coal gasification', be increased?

9.5 Describe the bulk preparation of dihydrogen by electrolytic method. What is the role of an electrolyte in this process ?

9.6 Complete the following reactions:

(i) $H_2(g) + M_mO_o(s) \xrightarrow{\Delta}$

(ii) $CO(g) + H_2(g) \xrightarrow[\text{catalyst}]{\Delta}$

(iii) $C_2H_2(g) - 3H_2O(g) \xrightarrow[\text{catalyst}]{\Delta}$

(iv) $Zn(s) + NaOH(aq) \xrightarrow{\text{heat}}$

9.7 Discuss the consequences of high enthalpy of H–H bond in terms of chemical reactivity of dihydrogen.

9.8 What do you understand by (i) electron-deficient, (ii) electron-precise, and (iii) electron-rich compounds of hydrogen? Provide justification with suitable examples.

9.9 What characteristics do you expect from an electron-deficient hydride with respect to its structure and chemical reactions?

9.10 Do you expect the carbon hydrides of the type (C_nH_{2n+2}) to act as 'Lewis' acid or base? Justify your answer.

9.11 What do you understand by the term "non-stoichiometric hydrides"? Do you expect this type of the hydrides to be formed by alkali metals? Justify your answer.

9.12 How do you expect the metallic hydrides to be useful for hydrogen storage? Explain.

9.13 How does the atomic hydrogen or oxy-hydrogen torch function for cutting and welding purposes ? Explain.

9.14 Among NH3, H_2O and HF, which would you expect to have highest magnitude of hydrogen bonding and why?

9.15 Saline hydrides are known to react with water violently producing fire. Can CO_2, a well known fire extinguisher, be used in this case? Explain.

9.16 Arrange the following

(i) CaH_2, BeH_2 and TiH_2 in order of increasing electrical conductance.

(ii) LiH, NaH and CsH in order of increasing ionic character.

(iii) H–H, D–D and F–F in order of increasing bond dissociation enthalpy.

(iv) NaH, MgH_2 and H_2O in order of increasing reducing property.

9.17 Compare the structures of H_2O and H_2O_2.

9.18 What do you understand by the term 'auto-protolysis' of water? What is its significance?

9.19 Consider the reaction of water with F_2 and suggest, in terms of oxidation and reduction, which species are oxidised/reduced.

9.20 Complete the following chemical reactions.

(i) $PbS(s) + H_2O_2(aq) \rightarrow$

(ii) $MnO_4(aq) + H_2O_2(aq) \rightarrow$

(iii) $CaO(s) + H_2O(g) \rightarrow$

(v) $AlCl_3(g) + H_2O(l) \rightarrow$

(vi) $Ca_3N_2(s) + H_2O(l) \rightarrow$

Classify the above into (a) hydrolysis, (b) redox and (c) hydration reactions.

9.21 Describe the structure of the common form of ice.

9.22 What causes the temporary and permanent hardness of water ?

9.23 Discuss the principle and method of softening of hard water by synthetic ion-exchange resins.

9.24 Write chemical reactions to show the amphoteric nature of water.

9.25 Write chemical reactions to justify that hydrogen peroxide can function as an oxidising as well as reducing agent.

9.26 What is meant by 'demineralised' water and how can it be obtained ?

9.27 Is demineralised or distilled water useful for drinking purposes? If not, how can it be made useful?

9.28 Describe the usefulness of water in biosphere and biological systems.

9.29 What properties of water make it useful as a solvent? What types of compound can it (i) dissolve, and (ii) hydrolyse ?

9.30 Knowing the properties of H_2O and D_2O, do you think that D_2O can be used for drinking purposes?

9.31 What is the difference between the terms 'hydrolysis' and 'hydration' ?

9.32 How can saline hydrides remove traces of water from organic compounds?

9.33 What do you expect the nature of hydrides is, if formed by elements of atomic numbers 15, 19, 23 and 44 with dihydrogen? Compare their behaviour towards water.

9.34 Do you expect different products in solution when aluminium(III) chloride and potassium chloride treated separately with (i) normal water (ii) acidified water, and (iii) alkaline water? Write equations wherever necessary.

9.35 How does H_2O_2 behave as a bleaching agent?

9.36 What do you understand by the terms:

(i) hydrogen economy (ii) hydrogenation (iii) 'syngas' (iv) water-gas shift reaction (v) fuel-cell ?

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Hydrogen

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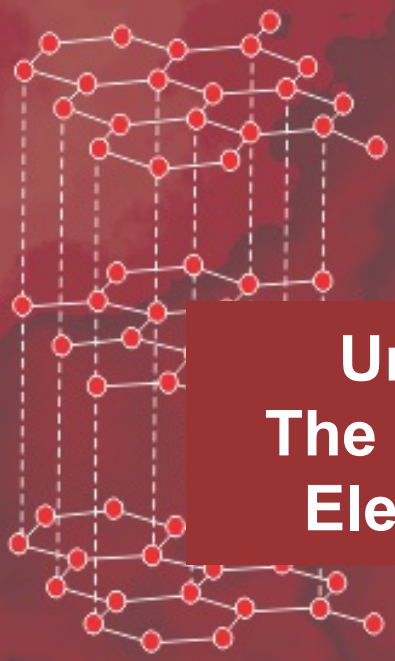
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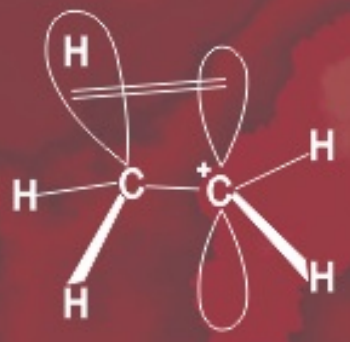
Textbook for Class XI



Unit 10
The s-Block Elements

Chemistry

Part II



11083CH10

Unit 10

The s-block elements

Objectives

After studying this unit, you will be able to

• describe the general charact-eristics of the alkali metals and their compounds;

• explain the general characteristics of the alkaline earth metals and their compounds;

• describe the manufacture, properties and uses of industrially important sodium and calcium compounds including Portland cement;

• appreciate the biological significance of sodium, potassium, magnesium and calcium.

*"**The first element of alkali and alkaline earth metals differs in many respects from the other members of the group.**"*

The s-block elements of the Periodic Table are those in which the last

electron enters the outermost s-orbital. As the s-orbital can accommodate only two electrons, two groups (1 & 2) belong to the s-block of the Periodic Table. Group 1 of the Periodic Table consists of the elements: lithium, sodium, potassium, rubidium, caesium and francium. They are collectively known as the alkali metals. These are so called because they form hydroxides on reaction with water which are strongly alkaline in nature. The elements of Group 2 include beryllium, magnesium, calcium, strontium, barium and radium. These elements with the exception of beryllium are commonly known as the alkaline earth metals. These are so called because their oxides and hydroxides are alkaline in nature and these metal oxides are found in the earth's crust*.

Among the alkali metals sodium and potassium are abundant and lithium, rubidium and caesium have much lower abundances (Table 10.1). Francium is highly radioactive; its longest-lived isotope 223Fr has a half-life of only 21 minutes. Of the alkaline earth metals calcium and magnesium rank fifth and sixth in abundance respectively in the earth's crust. Strontium and barium have much lower abundances. Beryllium is rare and radium is the rarest of all comprising only 10–10 per cent of igneous rocks† (Table 10.2, page 299).

The general electronic configuration of s-block elements is [noble gas]ns1 for alkali metals and [noble gas] ns2 for alkaline earth metals.

* The thin, rocky outer layer of the Earth is crust. † A type of rock formed from magma (molten rock) that has cooled and hardened.

Lithium and beryllium, the first elements of Group 1 and Group 2 respectively exhibit some properties which are different from those of the other members of the respective group. In these anomalous properties they resemble the second element of the following group. Thus, lithium shows similarities to magnesium and beryllium to aluminium in many of

their properties. This type of diagonal similarity is commonly referred to as diagonal relationship in the periodic table. The diagonal relationship is due to the similarity in ionic sizes and /or charge/radius ratio of the elements. Monovalent sodium and potassium ions and divalent magnesium and calcium ions are found in large proportions in biological fluids. These ions perform important biological functions such as maintenance of ion balance and nerve impulse conduction.

10.1 GROUP 1 ELEMENTS: ALKALI METALS

The alkali metals show regular trends in their physical and chemical properties with the increasing atomic number. The atomic, physical and chemical properties of alkali metals are discussed below.

10.1.1 Electronic Configuration

All the alkali metals have one valence electron, ns1 (Table 10.1) outside the noble gas core. The loosely held s-electron in the outermost valence shell of these elements makes them the most electropositive metals. They readily lose electron to give monovalent M^+ ions. Hence they are never found in free state in nature.

Element	Symbol	Electronic configuration
Lithium	Li	$1s^2 2s^1$
Sodium	Na	$1s^2 2s^2 2p^6 3s^1$
Potassium	K	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$
Rubidium	Rb	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 5s^1$
Caesium	Cs	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2$ $4p^6 4d^{10} 5s^2 5p^6 6s^1$ or [Xe] $6s^1$
Francium	Fr	[Rn] $7s^1$

10.1.2 Atomic and Ionic Radii

The alkali metal atoms have the largest sizes in a particular period of the

periodic table. With increase in atomic number, the atom becomes larger. The monovalent ions (M^+) are smaller than the parent atom. The atomic and ionic radii of alkali metals increase on moving down the group i.e., they increase in size while going from Li to Cs.

10.1.3 Ionization Enthalpy

The ionization enthalpies of the alkali metals are considerably low and decrease down the group from Li to Cs. This is because the effect of increasing size outweighs the increasing nuclear charge, and the outermost electron is very well screened from the nuclear charge.

10.1.4 Hydration Enthalpy

The hydration enthalpies of alkali metal ions decrease with increase in ionic sizes.

$Li^+ > Na^+ > K^+ > Rb^+ > Cs^+$

Li+ has maximum degree of hydration and for this reason lithium salts are mostly hydrated, e.g., $LiCl \cdot 2H_2O$

10.1.5 Physical Properties

All the alkali metals are silvery white, soft and light metals. Because of the large size, these elements have low density which increases down the group from Li to Cs. However, potassium is lighter than sodium. The melting and boiling points of the alkali metals are low indicating weak metallic bonding due to the presence of only a single valence electron in them. The alkali metals and their salts impart characteristic colour to an oxidizing flame. This is because the heat from the flame excites the outermost orbital electron to a higher energy level. When the excited

electron comes back to the ground state, there is emission of radiation in the visible region of the spectrum as given below:

Metal	Li	Na	K	Rb	Cs
Colour	Crimson red	Yellow	Violet	Red violet	Blue
λ/nm	670.8	589.2	766.5	780.0	455.5

Alkali metals can therefore, be detected by the respective flame tests and can be determined by flame photometry or atomic absorption spectroscopy. These elements when irradiated with light, the light energy absorbed may be sufficient to make an atom lose electron. This property makes caesium and potassium useful as electrodes in photoelectric cells.

Table 10.1 Atomic and Physical Properties of the Alkali Metals

Property	Lithium Li	Sodium Na	Potassium K	Rubidium Rb	Caesium Cs	Francium Fr
Atomic number	3	11	19	37	55	87
Atomic mass (g mol^{-1})	6.94	22.99	39.10	85.47	132.91	(223)
Electronic configuration	[He] $2s^1$	[Ne] $3s^1$	[Ar] $4s^1$	[Kr] $5s^1$	[Xe] $6s^1$	[Rn] $7s^1$
Ionization enthalpy / kJ mol^{-1}	520	496	419	403	376	~375
Hydration enthalpy/kJ mol^{-1}	–506	–406	–330	–310	–276	–
Metallic radius / pm	152	186	227	248	265	–
Ionic radius M^+ / pm	76	102	138	152	167	(180)
m.p. / K	454	371	336	312	302	–
b.p / K	1615	1156	1032	961	944	–
Density / g cm^{-3}	0.53	0.97	0.86	1.53	1.90	–
Standard potentials $E^{\ominus}$/ V for (M^+ / M)	–3.04	–2.714	–2.925	–2.930	–2.927	–
Occurrence in lithosphere†	18*	2.27**	1.84**	78-12*	2-6*	~ 10^{-18} *

*ppm (part per million), ** percentage by weight; † Lithosphere: The Earth's outer layer: its crust and part of the upper mantle

10.1.6 Chemical Properties

The alkali metals are highly reactive due to their large size and low ionization enthalpy. The reactivity of these metals increases down the group.

(i) Reactivity towards air: The alkali metals tarnish in dry air due to the formation of their oxides which in turn react with moisture to form hydroxides. They burn vigorously in oxygen forming oxides. Lithium forms monoxide, sodium forms peroxide, the other metals form superoxides. The superoxide O_2^- ion is stable only in the presence of large cations such as K, Rb, Cs.

$$4\,Li + O_2 \rightarrow 2\,Li_2O\ (oxide)$$

$$2\,Na + O_2 \rightarrow Na_2O_2\ (peroxide)$$

$$M + O_2 \rightarrow MO_2\ (superoxide)$$

(M = K, Rb, Cs)

In all these oxides the oxidation state of the alkali metal is +1. Lithium shows exceptional behaviour in reacting directly with nitrogen of air to form the nitride, Li3N as well. Because of their high reactivity towards air and water, alkali metals are normally kept in kerosene oil.

Problem 10.1

What is the oxidation state of K in KO_2?

Solution

The superoxide species is represented as O_2^-; since the compound is neutral, therefore, the oxidation state of potassium is +1.

(ii) Reactivity towards water: The alkali metals react with water to form hydroxide and dihydrogen.

$$2\,M + 2H_2O \rightarrow 2\,M^+ + 2\,OH^- + H_2$$

(M = an alkali metal)

It may be noted that although lithium has most negative Ẽ value (Table 10.1), its reaction with water is less vigorous than that of sodium which has the least negative Ẽ value among the alkali metals. This behaviour of lithium is attributed to its small size and very high hydration energy. Other metals of the group react explosively with water.

They also react with proton donors such as alcohol, gaseous ammonia and alkynes.

(iii) Reactivity towards dihydrogen: The alkali metals react with dihydrogen at about 673K (lithium at 1073K) to form hydrides. All the alkali metal hydrides are ionic solids with high melting points.

$$2\,M + H_2 \rightarrow 2\,M^+H^-$$

(iv) Reactivity towards halogens: The alkali metals readily react vigorously with halogens to form ionic halides, M^+X^-. However, lithium halides are somewhat covalent. It is because of the high polarisation capability of lithium ion (The distortion of electron cloud of the anion by the cation is called polarisation). The Li^+ ion is very small in size and has high tendency to distort electron cloud around the negative halide ion.

Since anion with large size can be easily distorted, among halides, lithium iodide is the most covalent in nature.

(v) Reducing nature: The alkali metals are strong reducing agents, lithium being the most and sodium the least powerful
(Table 10.1). The standard electrode potential (Ẽ) which measures the reducing power represents the overall change :

$$M(s) \rightarrow M(g) \qquad \text{sublimation enthalpy}$$
$$M(g) \rightarrow M^+(g) + e^- \qquad \text{ionization enthalpy}$$
$$M^+(g) + H_2O \rightarrow M^+(aq) \quad \text{hydration enthalpy}$$

With the small size of its ion, lithium has the highest hydration enthalpy which accounts for its high negative Ẽ value and its high reducing power.

Problem 10.2

The Ẽ for Cl_2/Cl^- is +1.36, for I_2/I^- is
+ 0.53, for Ag^+ /Ag is +0.79, Na^+ /Na is
–2.71 and for Li^+ /Li is – 3.04. Arrange the following ionic species in decreasing order of reducing strength:

I^-, Ag, Cl^-, Li, Na

Solution

The order is Li > Na > I^- > Ag > Cl^-

(vi) Solutions in liquid ammonia: The alkali metals dissolve in liquid ammonia giving deep blue solutions which are conducting in nature.

$$M + (x + y)NH_3 \rightarrow [M(NH_3)_x]^+ + [e(NH_3)_y]^-$$

The blue colour of the solution is due to the ammoniated electron which absorbs energy in the visible region of light and thus imparts blue colour to the solution. The solutions are paramagnetic and on standing slowly liberate hydrogen resulting in the formation of amide.

$$M^{+}_{(am)} + e^{-} + NH_3(l) \rightarrow MNH_{2(am)} + \tfrac{1}{2}H_2(g)$$

(where 'am' denotes solution in ammonia.)

In concentrated solution, the blue colour changes to bronze colour and becomes diamagnetic.

10.1.7 Uses

Lithium metal is used to make useful alloys, for example with lead to make 'white metal' bearings for motor engines, with aluminium to make aircraft parts, and with magnesium to make armour plates. It is used in thermonuclear reactions. Lithium is also used to make electrochemical cells. Sodium is used to make a Na/Pb alloy needed to make PbEt4 and $PbMe_4$. These organolead compounds were earlier used as anti-knock additives to petrol, but nowadays vehicles use lead-free petrol. Liquid sodium metal is used as a coolant in fast breeder nuclear reactors. Potassium has a vital role in biological systems. Potassium chloride is used as a fertilizer. Potassium hydroxide is used in the manufacture of soft soap. It is also used as an excellent absorbent of carbon dioxide. Caesium is used in devising photoelectric cells.

10.2 GENERAL CHARACTERISTICS OF THE COMPOUNDS OF THE ALKALI METALS

All the common compounds of the alkali metals are generally ionic in nature. General characteristics of some of their compounds are discussed here.

10.2.1 Oxides and Hydroxides

On combustion in excess of air, lithium forms mainly the oxide, Li_2O (plus some peroxide Li_2O_2), sodium forms the peroxide, Na_2O_2 (and some superoxide NaO_2) whilst potassium, rubidium and caesium form the superoxides, MO_2. Under appropriate conditions pure compounds M_2O, M_2O_2 and MO_2 may be prepared. The increasing stability of the peroxide or superoxide, as the size of the metal ion increases, is due to the stabilisation of large anions by larger cations through lattice energy effects. These oxides are easily hydrolysed by water to form the hydroxides according to the following reactions :

$$M_2O + H_2O \rightarrow 2M^+ + 2OH^-$$

$$M_2O_2 + 2H_2O \rightarrow 2M^+ + 2\,OH^- + H_2O_2$$

$$2\,MO_2 + 2H_2O \rightarrow 2M^+ + 2\,OH^- + H_2O_2 + O_2$$

The oxides and the peroxides are colourless when pure, but the superoxides are yellow or orange in colour. The superoxides are also paramagnetic. Sodium peroxide is widely used as an oxidising agent in inorganic chemistry.

Problem 10.3

Why is KO_2 paramagnetic ?

Solution

The superoxide O_2^- is paramagnetic because of one unpaired electron in π*2p molecular orbital.

The hydroxides which are obtained by the reaction of the oxides with water are all white crystalline solids. The alkali metal hydroxides are the strongest of all bases and dissolve freely in water with evolution of much heat on account of intense hydration.

10.2.2 Halides

The alkali metal halides, MX, (X=F,Cl,Br,I) are all high melting, colourless crystalline solids. They can be prepared by the reaction of the appropriate oxide, hydroxide or carbonate with aqueous hydrohalic acid (HX). All of these halides have high negative enthalpies of formation; the $\Delta f \tilde{H}$ values for fluorides become less negative as we go down the group, whilst the reverse is true for $\Delta f \tilde{H}$ for chlorides, bromides and iodides. For a given metal $\Delta f \tilde{H}$ always becomes less negative from fluoride to iodide.

The melting and boiling points always follow the trend: fluoride > chloride > bromide > iodide. All these halides are soluble in water. The low solubility of LiF in water is due to its high lattice enthalpy whereas the low solubility of CsI is due to smaller hydration enthalpy of its two ions. Other halides of lithium are soluble in ethanol, acetone and ethylacetate; LiCl is soluble in pyridine also.

10.2.3 Salts of Oxo-Acids

Oxo-acids are those in which the acidic proton is on a hydroxyl group with an oxo group attached to the same atom e.g., carbonic acid, H_2CO_3 ($OC(OH)_2$; sulphuric acid, H_2SO_4 ($O_2S(OH)_2$). The alkali metals form salts with all the oxo-acids. They are generally soluble in water and thermally stable. Their carbonates (M_2CO_3) and in most cases the hydrogencarbonates ($MHCO_3$) also are highly stable to heat. As the

electropositive character increases down the group, the stability of the carbonates and hydorgencarbonates increases. Lithium carbonate is not so stable to heat; lithium being very small in size polarises a large CO_3^{2-} ion leading to the formation of more stable Li_2O and CO_2. Its hydrogencarbonate does not exist as a solid.

10.3 ANOMALOUS PROPERTIES OF LITHIUM

The anomalous behaviour of lithium is due to the : (i) exceptionally small size of its atom and ion, and (ii) high polarising power (i.e., charge/radius ratio). As a result, there is increased covalent character of lithium compounds which is responsible for their solubility in organic solvents. Further, lithium shows diagonal relationship to magnesium which has been discussed subsequently.

10.3.1 Points of Difference between Lithium and other Alkali Metals

(i) Lithium is much harder. Its m.p. and b.p. are higher than the other alkali metals.

(ii) Lithium is least reactive but the strongest reducing agent among all the alkali metals. On combustion in air it forms mainly monoxide, Li_2O and the nitride, Li_3N unlike other alkali metals.

(iii) LiCl is deliquescent and crystallises as a hydrate, $LiCl.2H_2O$ whereas other alkali metal chlorides do not form hydrates.

(iv) Lithium hydrogencarbonate is not obtained in the solid form while all other elements form solid hydrogencarbonates.

(v) Lithium unlike other alkali metals forms no ethynide on reaction with

ethyne.

(vi) Lithium nitrate when heated gives lithium oxide, Li_2O, whereas other alkali metal nitrates decompose to give the corresponding nitrite.

$$4LiNO_3 \rightarrow 2Li_2O + 4NO_2 + O_2$$

$$2NaNO_3 \rightarrow 2NaNO_2 + O_2$$

(vii) LiF and Li_2O are comparatively much less soluble in water than the corresponding compounds of other alkali metals.

10.3.2 Points of Similarities between Lithium and Magnesium

The similarity between lithium and magnesium is particularly striking and arises because of their similar sizes : atomic radii, Li = 152 pm, Mg = 160 pm; ionic radii : Li^+ = 76 pm,

Mg^{2+}= 72 pm. The main points of similarity are:

(i) Both lithium and magnesium are harder and lighter than other elements in the respective groups.

(ii) Lithium and magnesium react slowly with water. Their oxides and hydroxides are much less soluble and their hydroxides decompose on heating. Both form a nitride, Li_3N and Mg_3N_2, by direct combination with nitrogen.

(iii) The oxides, Li_2O and MgO do not combine with excess oxygen to give any superoxide.

(iv) The carbonates of lithium and magnesium decompose easily on heating to

form the oxides and CO_2. Solid hydrogencarbonates are not formed by lithium and magnesium.

(v) Both LiCl and $MgCl_2$ are soluble in ethanol.

(vi) Both LiCl and $MgCl_2$ are deliquescent and crystallise from aqueous solution as hydrates, $LiCl \cdot 2H_2O$ and $MgCl_2 \cdot 8H_2O$.

10.4 SOME IMPORTANT COMPOUNDS OF SODIUM

Industrially important compounds of sodium include sodium carbonate, sodium hydroxide, sodium chloride and sodium bicarbonate. The large scale production of these compounds and their uses are described below:

Sodium Carbonate (Washing Soda), $Na_2CO_3 \cdot 10H_2O$

Sodium carbonate is generally prepared by Solvay Process. In this process, advantage is taken of the low solubility of sodium hydrogencarbonate whereby it gets precipitated in the reaction of sodium chloride with ammonium hydrogencarbonate. The latter is prepared by passing CO_2 to a concentrated solution of sodium chloride saturated with ammonia, where ammonium carbonate followed by ammonium hydrogencarbonate are formed. The equations for the complete process may be written as :

$$2\,NH_3 + H_2O + CO_2 \rightarrow (NH_4)_2\,CO_3$$

$$(NH_4)_2\,CO_3 + H_2O + CO_2 \rightarrow 2\,NH_4HCO_3$$

$$NH_4HCO_3 + NaCl \rightarrow NH_4Cl + NaHCO_3$$

Sodium hydrogencarbonate crystal separates. These are heated to give sodium carbonate.

$$2\,NaHCO_3 \rightarrow Na_2CO_3 + CO_2 + H_2O$$

In this process NH_3 is recovered when the solution containing NH_4Cl is treated with $Ca(OH)_2$. Calcium chloride is obtained as a by-product.

$$2\,NH_4Cl + Ca(OH)_2 \rightarrow 2\,NH_3 + CaCl_2 + H_2O$$

It may be mentioned here that Solvay process cannot be extended to the manufacture of potassium carbonate because potassium hydrogencarbonate is too soluble to be precipitated by the addition of ammonium hydrogencarbonate to a saturated solution of potassium chloride.

Properties : Sodium carbonate is a white crystalline solid which exists as a decahydrate, $Na_2CO_3 \cdot 10H_2O$. This is also called washing soda. It is readily soluble in water. On heating, the decahydrate loses its water of crystallisation to form monohydrate. Above 373K, the monohydrate becomes completely anhydrous and changes to a white powder called soda ash.

$$Na_2CO_3 \cdot 10H_2O \xrightarrow{375K} Na_2CO_3 \cdot H_2O + 9H_2O$$

$$Na_2CO_3 \cdot H_2O \xrightarrow{>373K} Na_2CO_3 + H_2O$$

Carbonate part of sodium carbonate gets hydrolysed by water to form an alkaline solution.

$$CO_3^{2-} + H_2O \rightarrow HCO_3^- + OH^-$$

Uses:

(i) It is used in water softening, laundering and cleaning.

(ii) It is used in the manufacture of glass, soap, borax and caustic soda.

(iii) It is used in paper, paints and textile industries.

(iv) It is an important laboratory reagent both in qualitative and quantitative analysis.

Sodium Chloride, NaCl

The most abundant source of sodium chloride is sea water which contains 2.7 to 2.9% by mass of the salt. In tropical countries like India, common salt is generally obtained by evaporation of sea water. Approximately 50 lakh tons of salt are produced annually in India by solar evaporation. Crude sodium chloride, generally obtained by crystallisation of brine solution, contains sodium sulphate, calcium sulphate, calcium chloride and magnesium chloride as impurities. Calcium chloride, $CaCl_2$, and magnesium chloride, $MgCl_2$ are impurities because they are deliquescent (absorb moisture easily from the atmosphere). To obtain pure sodium chloride, the crude salt is dissolved in minimum amount of water and filtered to remove insoluble impurities. The solution is then saturated with hydrogen chloride gas. Crystals of pure sodium chloride separate out. Calcium and magnesium chloride, being more soluble than sodium chloride, remain in solution.

Sodium chloride melts at 1081K. It has a solubility of 36.0 g in 100 g of water at 273 K. The solubility does not increase appreciably with increase in temperature.

Uses :

(i) It is used as a common salt or table salt for domestic purpose.

(ii) It is used for the preparation of Na_2O_2, NaOH and Na_2CO_3.

Sodium Hydroxide (Caustic Soda), NaOH

Sodium hydroxide is generally prepared commercially by the electrolysis of sodium chloride in Castner-Kellner cell. A brine solution is electrolysed using a mercury cathode and a carbon anode. Sodium metal discharged at the cathode combines with mercury to form sodium amalgam. Chlorine gas is evolved at the anode.

$$\text{Cathode}: \ Na^+ \ + \ e^- \xrightarrow{Hg} Na - \text{amalgam}$$

$$\text{Anode}: Cl^- \rightarrow \frac{1}{2} Cl_2 + e^-$$

The amalgam is treated with water to give sodium hydroxide and hydrogen gas.

$2Na\text{-amalgam} + 2H_2O \rightarrow 2NaOH + 2Hg + H_2$

Sodium hydroxide is a white, translucent solid. It melts at 591 K. It is readily soluble in water to give a strong alkaline solution. Crystals of sodium hydroxide are deliquescent. The sodium hydroxide solution at the surface reacts with the CO_2 in the atmosphere to form Na_2CO_3.

Uses: It is used in (i) the manufacture of soap, paper, artificial silk and a number of chemicals, (ii) in petroleum refining, (iii) in the purification of bauxite, (iv) in the textile industries for mercerising cotton fabrics, (v) for the preparation of pure fats and oils, and (vi) as a laboratory reagent.

Sodium Hydrogencarbonate (Baking Soda), $NaHCO_3$

Sodium hydrogencarbonate is known as baking soda because it decomposes on heating to generate bubbles of carbon dioxide (leaving holes in cakes or pastries and making them light and fluffy).

Sodium hydrogencarbonate is made by saturating a solution of sodium

carbonate with carbon dioxide. The white crystalline powder of sodium hydrogencarbonate, being less soluble, gets separated out.

$$Na_2CO_3 + H_2O + CO_2 \rightarrow 2\,NaHCO_3$$

Sodium hydrogencarbonate is a mild antiseptic for skin infections. It is used in fire extinguishers.

10.5 BIOLOGICAL IMPORTANCE OF SODIUM AND POTASSIUM

A typical 70 kg man contains about 90 g of Na and 170 g of K compared with only 5 g of iron and 0.06 g of copper.

Sodium ions are found primarily on the outside of cells, being located in blood plasma and in the interstitial fluid which surrounds the cells. These ions participate in the transmission of nerve signals, in regulating the flow of water across cell membranes and in the transport of sugars and amino acids into cells. Sodium and potassium, although so similar chemically, differ quantitatively in their ability to penetrate cell membranes, in their transport mechanisms and in their efficiency to activate enzymes. Thus, potassium ions are the most abundant cations within cell fluids, where they activate many enzymes, participate in the oxidation of glucose to produce ATP and, with sodium, are responsible for the transmission of nerve signals.

There is a very considerable variation in the concentration of sodium and potassium ions found on the opposite sides of cell membranes. As a typical example, in blood plasma, sodium is present to the extent of 143 $mmolL^{-1}$, whereas the potassium level is only 5 $mmolL^{-1}$ within the red blood cells. These concentrations change to 10 $mmolL^{-1}$ (Na^+) and 105 $mmolL^{-1}$ (K^+). These ionic gradients demonstrate that a discriminatory

mechanism, called the sodium-potassium pump, operates across the cell membranes which consumes more than one-third of the ATP used by a resting animal and about 15 kg per 24 h in a resting human.

10.6 GROUP 2 ELEMENTS : ALKALINE EARTH METALS

The group 2 elements comprise beryllium, magnesium, calcium, strontium, barium and radium. They follow alkali metals in the periodic table. These (except beryllium) are known as alkaline earth metals. The first element beryllium differs from the rest of the members and shows diagonal relationship to aluminium. The atomic and physical properties of the alkaline earth metals are shown in Table 10.2.

10.6.1 Electronic Configuration

These elements have two electrons in the s -orbital of the valence shell (Table 10.2). Their general electronic configuration may be represented as [noble gas] ns2. Like alkali metals, the compounds of these elements are also predominantly ionic.

Element	Symbol	Electronic configuration
Beryllium	Be	$1s^2 2s^2$
Magnesium	Mg	$1s^2 2s^2 2p^6 3s^2$
Calcium	Ca	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$
Strontium	Sr	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 5s^2$
Barium	Ba	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^6 6s^2$ or $[Xe]6s^2$
Radium	Ra	$[Rn]7s^2$

10.6.2 Atomic and Ionic Radii

The atomic and ionic radii of the alkaline earth metals are smaller than

those of the corresponding alkali metals in the same periods. This is due to the increased nuclear charge in these elements. Within the group, the atomic and ionic radii increase with increase in atomic number.

Table 10.2 Atomic and Physical Properties of the Alkaline Earth Metals

Property	Beryllium Be	Magnesium Mg	Calcium Ca	Strontium Sr	Barium Ba	Radium Ra
Atomic number	4	12	20	38	56	88
Atomic mass (g mol^{-1})	9.01	24.31	40.08	87.62	137.33	226.03
Electronic configuration	[He] $2s^2$	[Ne] $3s^2$	[Ar] $4s^2$	[Kr] $5s^2$	[Xe] $6s^2$	[Rn] $7s^2$
Ionization enthalpy (I) / kJ mol^{-1}	899	737	590	549	503	509
Ionization enthalpy (II) /kJ mol^{-1}	1757	1450	1145	1064	965	979
Hydration enthalpy (kJ/mol)	– 2494	– 1921	–1577	– 1443	– 1305	–
Metallic radius / pm	111	160	197	215	222	–
Ionic radius M^{2+} / pm	31	72	100	118	135	148
m.p. / K	1560	924	1124	1062	1002	973
b.p / K	2745	1363	1767	1655	2078	(1973)
Density / g cm^{-3}	1.84	1.74	1.55	2.63	3.59	(5.5)
Standard potential $E^{\ominus}$ / V for (M^{2+}/ M)	–1.97	–2.36	–2.84	–2.89	– 2.92	–2.92
Occurrence in lithosphere	2*	2.76**	4.6**	384*	390 *	10^{-6}*

*ppm (part per million); ** percentage by weight

10.6.3 Ionization Enthalpies

The alkaline earth metals have low ionization enthalpies due to fairly large size of the atoms. Since the atomic size increases down the group, their ionization enthalpy decreases (Table 10.2). The first ionisation enthalpies of the alkaline earth metals are higher than those of the corresponding Group 1 metals. This is due to their small size as compared to the corresponding alkali metals. It is interesting to note that

the second ionisation enthalpies of the alkaline earth metals are smaller than those of the corresponding alkali metals.

10.6.4 Hydration Enthalpies

Like alkali metal ions, the hydration enthalpies of alkaline earth metal ions decrease with increase in ionic size down the group.

$$Be^{2+} > Mg^{2+} > Ca^{2+} > Sr^{2+} > Ba^{2+}$$

The hydration enthalpies of alkaline earth metal ions are larger than those of alkali metal ions. Thus, compounds of alkaline earth metals are more extensively hydrated than those of alkali metals, e.g., $MgCl_2$ and $CaCl_2$ exist as $MgCl_2.6H_2O$ and $CaCl_2 \cdot 6H_2O$ while NaCl and KCl do not form such hydrates.

10.6.5 Physical Properties

The alkaline earth metals, in general, are silvery white, lustrous and relatively soft but harder than the alkali metals. Beryllium and magnesium appear to be somewhat greyish. The melting and boiling points of these metals are higher than the corresponding alkali metals due to smaller sizes. The trend is, however, not systematic. Because of the low ionisation enthalpies, they are strongly electropositive in nature. The electropositive character increases down the group from Be to Ba. Calcium, strontium and barium impart characteristic brick red, crimson and apple green colours respectively to the flame. In flame the electrons are excited to higher energy levels and when they drop back to the ground state, energy is emitted in the form of visible light. The electrons in beryllium and magnesium are too strongly bound to get excited by flame. Hence, these elements do not impart any colour to the flame. The

flame test for Ca, Sr and Ba is helpful in their detection in qualitative analysis and estimation by flame photometry. The alkaline earth metals like those of alkali metals have high electrical and thermal conductivities which are typical characteristics of metals.

10.6.6 Chemical Properties

The alkaline earth metals are less reactive than the alkali metals. The reactivity of these elements increases on going down the group.

(i) Reactivity towards air and water: Beryllium and magnesium are kinetically inert to oxygen and water because of the formation of an oxide film on their surface. However, powdered beryllium burns brilliantly on ignition in air to give BeO and Be3N2. Magnesium is more electropositive and burns with dazzling brilliance in air to give MgO and Mg_3N_2. Calcium, strontium and barium are readily attacked by air to form the oxide and nitride. They also react with water with increasing vigour even in cold to form hydroxides.

(ii) Reactivity towards the halogens: All the alkaline earth metals combine with halogen at elevated temperatures forming their halides.

$$M + X_2 \rightarrow MX_2 \, (X = F, Cl, Br, I)$$

Thermal decomposition of (NH4)2BeF4 is the best route for the preparation of BeF_2, and $BeCl_2$ is conveniently made from the oxide.

$$BeO + C + Cl_2 \xrightleftharpoons{600-800K} BeCl_2 + CO$$

(iii) Reactivity towards hydrogen: All the elements except beryllium combine with hydrogen upon heating to form their hydrides, MH_2.

BeH_2, however, can be prepared by the reaction of $BeCl_2$ with $LiAlH_4$.

$$2BeCl_2 + LiAlH_4 \rightarrow 2BeH_2 + LiCl + AlCl_3$$

(iv) Reactivity towards acids: The alkaline earth metals readily react with acids liberating dihydrogen.

$M + 2HCl \rightarrow MCl_2 + H_2$

(v) Reducing nature: Like alkali metals, the alkaline earth metals are strong reducing agents. This is indicated by large negative values of their reduction potentials (Table 10.2). However their reducing power is less than those of their corresponding alkali metals. Beryllium has less negative value compared to other alkaline earth metals. However, its reducing nature is due to large hydration energy associated with the small size of Be^{2+} ion and relatively large value of the atomization enthalpy of the metal.

(vi) Solutions in liquid ammonia: Like alkali metals, the alkaline earth metals dissolve in liquid ammonia to give deep blue black solutions forming ammoniated ions.

$$M + (x+y)NH_3 \rightarrow \left[M(NH_3)_x\right]^{2+} + 2\left[e(NH_3)_y\right]^-$$

From these solutions, the ammoniates, $[M(NH_3)_6]^{2+}$ can be recovered.

10.6.7 Uses

Beryllium is used in the manufacture of alloys. Copper-beryllium alloys are used in the preparation of high strength springs. Metallic beryllium is used for making windows of X-ray tubes. Magnesium forms alloys with aluminium, zinc, manganese and tin. Magnesium-aluminium alloys being light in mass are used in air-craft construction. Magnesium (powder and ribbon) is used in flash powders and bulbs, incendiary bombs and signals. A suspension of magnesium hydroxide in water (called milk of

magnesia) is used as antacid in medicine. Magnesium carbonate is an ingredient of toothpaste. Calcium is used in the extraction of metals from oxides which are difficult to reduce with carbon. Calcium and barium metals, owing to their reactivity with oxygen and nitrogen at elevated temperatures, have often been used to remove air from vacuum tubes. Radium salts are used in radiotherapy, for example, in the treatment of cancer.

10.7 GENERAL CHARACTERISTICS OF COMPOUNDS OF THE ALKALINE EARTH METALS

The dipositive oxidation state (M^{2+}) is the predominant valence of Group 2 elements. The alkaline earth metals form compounds which are predominantly ionic but less ionic than the corresponding compounds of alkali metals. This is due to increased nuclear charge and smaller size. The oxides and other compounds of beryllium and magnesium are more covalent than those formed by the heavier and large sized members (Ca, Sr, Ba). The general characteristics of some of the compounds of alkali earth metals are described below.

(i) Oxides and Hydroxides: The alkaline earth metals burn in oxygen to form the monoxide, MO which, except for BeO, have rock-salt structure. The BeO is essentially covalent in nature. The enthalpies of formation of these oxides are quite high and consequently they are very stable to heat. BeO is amphoteric while oxides of other elements are ionic in nature. All these oxides except BeO are basic in nature and react with water to form sparingly soluble hydroxides.

$$MO + H_2O \rightarrow M(OH)_2$$

The solubility, thermal stability and the basic character of these

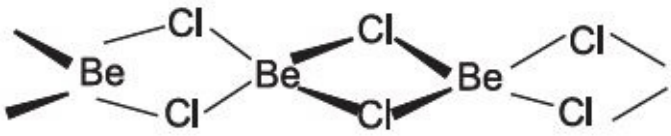
hydroxides increase with increasing atomic number from $Mg(OH)_2$ to $Ba(OH)_2$. The alkaline earth metal hydroxides are, however, less basic and less stable than alkali metal hydroxides. Beryllium hydroxide is amphoteric in nature as it reacts with acid and alkali both.

$$Be(OH)_2 + 2OH^- \rightarrow [Be(OH)_4]^{2-}$$

Beryllate ion

$$Be(OH)_2 + 2HCl + 2H_2O \rightarrow [Be(OH)_4]Cl_2$$

(ii) Halides: Except for beryllium halides, all other halides of alkaline earth metals are ionic in nature. Beryllium halides are essentially covalent and soluble in organic solvents. Beryllium chloride has a chain structure in the solid state as shown below:



In the vapour phase $BeCl_2$ tends to form a chloro-bridged dimer which dissociates into the linear monomer at high temperatures of the order of 1200 K. The tendency to form halide hydrates gradually decreases (for example, $MgCl_2 \cdot 8H_2O$, $CaCl_2 \cdot 6H_2O$, $SrCl_2 \cdot 6H_2O$ and $BaCl_2 \cdot 2H_2O$) down the group. The dehydration of hydrated chlorides, bromides and iodides of Ca, Sr and Ba can be achieved on heating; however, the corresponding hydrated halides of Be and Mg on heating suffer hydrolysis. The fluorides are relatively less soluble than the chlorides owing to their high lattice energies.

(iii) Salts of Oxoacids: The alkaline earth metals also form salts of oxoacids. Some of these are :

Carbonates: Carbonates of alkaline earth metals are insoluble in water

and can be precipitated by addition of a sodium or ammonium carbonate solution to a solution of a soluble salt of these metals. The solubility of carbonates in water decreases as the atomic number of the metal ion increases. All the carbonates decompose on heating to give carbon dioxide and the oxide. Beryllium carbonate is unstable and can be kept only in the atmosphere of CO_2. The thermal stability increases with increasing cationic size.

Sulphates: The sulphates of the alkaline earth metals are all white solids and stable to heat. $BeSO_4$, and $MgSO_4$ are readily soluble in water; the solubility decreases from $CaSO_4$ to $BaSO_4$. The greater hydration enthalpies of Be^{2+} and Mg^{2+} ions overcome the lattice enthalpy factor and therefore their sulphates are soluble in water.

Nitrates: The nitrates are made by dissolution of the carbonates in dilute nitric acid. Magnesium nitrate crystallises with six molecules of water, whereas barium nitrate crystallises as the anhydrous salt. This again shows a decreasing tendency to form hydrates with increasing size and decreasing hydration enthalpy. All of them decompose on heating to give the oxide like lithium nitrate.

$$2M(NO_3)_2 \rightarrow 2MO + 4NO_2 + O_2$$

(M = Be, Mg, Ca, Sr, Ba)

Problem 10.4

Why does the solubility of alkaline earth metal hydroxides in water increase down the group?

Solution

Among alkaline earth metal hydroxides, the anion being common the cationic radius will influence the lattice enthalpy. Since lattice enthalpy decreases much more than the hydration enthalpy with increasing

ionic size, the solubility increases as we go down the group.

Problem 10.5

Why does the solubility of alkaline earth metal carbonates and sulphates in water decrease down the group?

Solution

The size of anions being much larger compared to cations, the lattice enthalpy will remain almost constant within a particular group. Since the hydration enthalpies decrease down the group, solubility will decrease as found for alkaline earth metal carbonates and sulphates.

10.8 ANOMALOUS BEHAVIOUR OF BERYLLIUM

Beryllium, the first member of the Group 2 metals, shows anomalous behaviour as compared to magnesium and rest of the members. Further, it shows diagonal relationship to aluminium which is discussed subsequently.

(i) Beryllium has exceptionally small atomic and ionic sizes and thus does not compare well with other members of the group. Because of high ionisation enthalpy and small size it forms compounds which are largely covalent and get easily hydrolysed.

(ii) Beryllium does not exhibit coordination number more than four as in its valence shell there are only four orbitals. The remaining members of the group can have a coordination number of six by making use of d-orbitals.

(iii) The oxide and hydroxide of beryllium, unlike the hydroxides of other elements in the group, are amphoteric in nature.

10.8.1 Diagonal Relationship between Beryllium and

Aluminium

The ionic radius of Be^{2+} is estimated to be 31 pm; the charge/radius ratio is nearly the same as that of the Al^{3+} ion. Hence beryllium resembles aluminium in some ways. Some of the similarities are:

(i) Like aluminium, beryllium is not readily attacked by acids because of the presence of an oxide film on the surface of the metal.

(ii) Beryllium hydroxide dissolves in excess of alkali to give a beryllate ion, $[Be(OH)_4]^{2-}$ just as aluminium hydroxide gives aluminate ion, $[Al(OH)_4]^-$.

(iii) The chlorides of both beryllium and aluminium have Cl^- bridged chloride structure in vapour phase. Both the chlorides are soluble in organic solvents and are strong Lewis acids. They are used as Friedel Craft catalysts.

(iv) Beryllium and aluminium ions have strong tendency to form complexes, BeF_4^{2-}, AlF_6^{3-}.

10.9 SOME IMPORTANT COMPOUNDS OF CALCIUM

Important compounds of calcium are calcium oxide, calcium hydroxide, calcium sulphate, calcium carbonate and cement. These are industrially important compounds. The large scale preparation of these compounds and their uses are described below.

Calcium Oxide or Quick Lime, CaO

It is prepared on a commercial scale by heating limestone ($CaCO_3$) in a rotary kiln at 1070-1270 K.

$$CaCO_3 \xrightleftharpoons{heat} CaO + CO_2$$

The carbon dioxide is removed as soon as it is produced to enable the reaction to proceed to completion.

Calcium oxide is a white amorphous solid. It has a melting point of 2870 K. On exposure to atmosphere, it absorbs moisture and carbon dioxide.

$$CaO + H_2O \rightarrow Ca(OH)_2$$

$$CaO + CO_2 \rightarrow CaCO_3$$

The addition of limited amount of water breaks the lump of lime. This process is called slaking of lime. Quick lime slaked with soda gives solid sodalime. Being a basic oxide, it combines with acidic oxides at high temperature.

$$CaO + SiO_2 \rightarrow CaSiO_3$$

$$6CaO + P_4O_{10} \rightarrow 2Ca_3(PO_4)_2$$

Uses:

(i) It is an important primary material for manufacturing cement and is the cheapest form of alkali.

(ii) It is used in the manufacture of sodium carbonate from caustic soda.

(iii) It is employed in the purification of sugar and in the manufacture of dye stuffs.

Calcium Hydroxide (Slaked lime), $Ca(OH)_2$

Calcium hydroxide is prepared by adding water to quick lime, CaO.

It is a white amorphous powder. It is sparingly soluble in water. The aqueous solution is known as lime water and a suspension of slaked lime in water is known as milk of lime.

When carbon dioxide is passed through lime water it turns milky due to the formation of calcium carbonate.

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$$

On passing excess of carbon dioxide, the precipitate dissolves to form calcium hydrogencarbonate.

$$CaCO_3 + CO_2 + H_2O \rightarrow Ca(HCO_3)_2$$

Milk of lime reacts with chlorine to form hypochlorite, a constituent of bleaching powder.

$$2Ca(OH)_2 + 2Cl_2 \rightarrow \underset{\text{Bleaching powder}}{CaCl_2 + Ca(OCl)_2} + 2H_2O$$

Uses:

(i) It is used in the preparation of mortar, a building material.

(ii) It is used in white wash due to its disinfectant nature.

(iii) It is used in glass making, in tanning industry, for the preparation of bleaching powder and for purification of sugar.

Calcium Carbonate, $CaCO_3$

Calcium carbonate occurs in nature in several forms like limestone, chalk, marble etc. It can be prepared by passing carbon dioxide through slaked lime or by the addition of sodium carbonate to calcium chloride.

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$$

$$CaCl_2 + Na_2CO_3 \rightarrow CaCO_3 + 2NaCl$$

Excess of carbon dioxide should be avoided since this leads to the formation of water soluble calcium hydrogencarbonate.

Calcium carbonate is a white fluffy powder. It is almost insoluble in water. When heated to 1200 K, it decomposes to evolve carbon dioxide.

$$CaCO_3 \xrightarrow{1200\,K} CaO + CO_2$$

It reacts with dilute acid to liberate carbon dioxide.

$$CaCO_3 + 2HCl \rightarrow CaCl_2 + H_2O + CO_2$$

$$CaCO_3 + H_2SO_4 \rightarrow CaSO_4 + H_2O + CO_2$$

Uses:

It is used as a building material in the form of marble and in the manufacture of quick lime. Calcium carbonate along with magnesium carbonate is used as a flux in the extraction of metals such as iron. Specially precipitated $CaCO_3$ is extensively used in the manufacture of high quality paper. It is also used as an antacid, mild abrasive in tooth paste, a constituent of chewing gum, and a filler in cosmetics.

Calcium Sulphate (Plaster of Paris), $CaSO_4 \cdot ½\ H_2O$

It is a hemihydrate of calcium sulphate. It is obtained when gypsum, $CaSO_4 \cdot 2H_2O$, is heated to 393 K.

$$2(CaSO_4.2H_2O) \rightarrow 2(CaSO_4).H_2O + 3H_2O$$

Above 393 K, no water of crystallisation is left and anhydrous calcium sulphate, $CaSO_4$ is formed. This is known as ‘dead burnt plaster’.

It has a remarkable property of setting with water. On mixing with an adequate quantity of water it forms a plastic mass that gets into a hard solid in 5 to 15 minutes.

Uses:

The largest use of Plaster of Paris is in the building industry as well as plasters. It is used for immoblising the affected part of organ where there is a bone fracture or sprain. It is also employed in dentistry, in ornamental work and for making casts of statues and busts.

Cement: Cement is an important building material. It was first introduced in England in 1824 by Joseph Aspdin. It is also called Portland cement because it resembles with the natural limestone quarried in the Isle of Portland, England.

Cement is a product obtained by combining a material rich in lime, CaO with other material such as clay which contains silica, SiO_2 along with the oxides of aluminium, iron and magnesium. The average composition of Portland cement is : CaO, 50-60%; SiO_2, 20-25%; Al_2O_3, 5-10%; MgO, 2-3%; Fe_2O_3, 1-2% and SO_3, 1-2%. For a good quality cement, the ratio of silica (SiO_2) to alumina (Al_2O_3) should be between 2.5 and 4 and the ratio of lime (CaO) to the total of the oxides of silicon (SiO_2) aluminium (Al_2O_3) and iron (Fe_2O_3) should be as close as possible to 2.

The raw materials for the manufacture of cement are limestone and clay. When clay and lime are strongly heated together they fuse and react to form ‘cement clinker’. This clinker is mixed with 2-3% by weight of gypsum ($CaSO_4 \cdot 2H_2O$) to form cement. Thus important ingredients present in Portland cement are dicalcium silicate (Ca_2SiO_4) 26%, tricalcium silicate (Ca_3SiO_5) 51% and tricalcium aluminate ($Ca_3Al_2O_6$)

11%.

Setting of Cement: When mixed with water, the setting of cement takes place to give a hard mass. This is due to the hydration of the molecules of the constituents and their rearrangement. The purpose of adding gypsum is only to slow down the process of setting of the cement so that it gets sufficiently hardened.

Uses: Cement has become a commodity of national necessity for any country next to iron and steel. It is used in concrete and reinforced concrete, in plastering and in the construction of bridges, dams and buildings.

10.10 BIOLOGICAL IMPORTANCE OF MAGNESIUM AND CALCIUM

An adult body contains about 25 g of Mg and 1200 g of Ca compared with only 5 g of iron and 0.06 g of copper. The daily requirement in the human body has been estimated to be 200 – 300 mg.

All enzymes that utilise ATP in phosphate transfer require magnesium as the cofactor. The main pigment for the absorption of light in plants is chlorophyll which contains magnesium. About 99 % of body calcium is present in bones and teeth. It also plays important roles in neuromuscular function, interneuronal transmission, cell membrane integrity and blood coagulation. The calcium concentration in plasma is regulated at about 100 mgL^{-1}. It is maintained by two hormones: calcitonin and parathyroid hormone. Do you know that bone is not an inert and unchanging substance but is continuously being solubilised and redeposited to the extent of 400 mg per day in man? All this calcium passes through the plasma.

SUMMARY

The **s-Block** of the periodic table constitutes **Group1** (alkali metals) and **Group 2** (alkaline earth metals). They are so called because their oxides and hydroxides are alkaline in nature. The alkali metals are characterised by one s-electron and the alkaline earth metals by two s-electrons in the valence shell of their atoms. These are highly reactive metals forming monopositive **(M^+)** and dipositve **(M^{2+})** ions respectively.

There is a regular trend in the physical and chemical properties of the alkali metal with increasing atomic numbers. The **atomic and ionic** sizes increase and the ionization enthalpies decrease systematically down the group. Somewhat similar trends are observed among the properties of the alkaline earth metals.

The first element in each of these groups, lithium in Group 1 and beryllium in Group 2 shows similarities in properties to the second member of the next group. Such similarities are termed as the **'diagonal relationship'** in the periodic table. As such these elements are anomalous as far as their group characteristics are concerned.

The alkali metals are silvery white, soft and low melting. They are highly reactive. The compounds of alkali metals are predominantly ionic. Their oxides and hydroxides are soluble in water forming strong alkalies. Important compounds of sodium includes sodium carbonate, sodium chloride, sodium hydroxide and sodium hydrogencarbonate. Sodium hydroxide is manufactured by **Castner-Kellner** process and sodium carbonate by **Solvay** process.

The chemistry of alkaline earth metals is very much like that of the alkali metals. However, some differences arise because of reduced atomic and ionic sizes and increased cationic charges in case of alkaline earth metals. Their oxides and hydroxides are less basic than the alkali metal oxides and hydroxides. Industrially important compounds of calcium include calcium oxide (lime), calcium hydroxide (slaked lime), calcium sulphate **(Plaster of Paris)**, calcium carbonate (limestone) and cement. **Portland cement** is an important constructional material. It is manufactured by heating a pulverised

mixture of limestone and clay in a rotary kiln. The clinker thus obtained is mixed with some gypsum (2-3%) to give a fine powder of cement. All these substances find variety of uses in different areas.

Monovalent sodium and potassium ions and divalent magnesium and calcium ions are found in large proportions in **biological fluids**. These ions perform important biological functions such as maintenance of ion balance and nerve impulse conduction.

Exercises

10.1 What are the common physical and chemical features of alkali metals ?

10.2 Discuss the general characteristics and gradation in properties of alkaline earth metals.

10.3 Why are alkali metals not found in nature ?

10.4 Find out the oxidation state of sodium in Na_2O_2.

10.5 Explain why is sodium less reactive than potassium.

10.6 Compare the alkali metals and alkaline earth metals with respect to (i) ionisation enthalpy (ii) basicity of oxides and (iii) solubility of hydroxides.

10.7 In what ways lithium shows similarities to magnesium in its chemical behaviour?

10.8 Explain why can alkali and alkaline earth metals not be obtained by chemical reduction methods?

10.9 Why are potassium and caesium, rather than lithium used in photoelectric cells?

10.10 When an alkali metal dissolves in liquid ammonia the solution can acquire different colours. Explain the reasons for this type of colour change.

10.11 Beryllium and magnesium do not give colour to flame whereas other alkaline earth metals do so. Why ?

10.12 Discuss the various reactions that occur in the Solvay process.

10.13 Potassium carbonate cannot be prepared by Solvay process. Why ?

10.14 Why is Li_2CO_3 decomposed at a lower temperature whereas Na_2CO_3 at higher temperature?

10.15 Compare the solubility and thermal stability of the following compounds of the alkali metals with those of the alkaline earth metals. (a) Nitrates (b) Carbonates (c) Sulphates.

10.16 Starting with sodium chloride how would you proceed to prepare (i) sodium metal (ii) sodium hydroxide (iii) sodium peroxide (iv) sodium carbonate ?

10.17 What happens when (i) magnesium is burnt in air (ii) quick lime is heated with silica (iii) chlorine reacts with slaked lime (iv) calcium nitrate is heated ?

10.18 Describe two important uses of each of the following : (i) caustic soda (ii) sodium carbonate (iii) quicklime.

10.19 Draw the structure of (i) $BeCl_2$ (vapour) (ii) BeCl2 (solid).

10.20 The hydroxides and carbonates of sodium and potassium are easily soluble in water while the corresponding salts of magnesium and calcium are sparingly soluble in water. Explain.

10.21 Describe the importance of the following : (i) limestone (ii) cement (iii) plaster of paris.

10.22 Why are lithium salts commonly hydrated and those of the other alkali ions usually anhydrous?

10.23 Why is LiF almost insoluble in water whereas LiCl soluble not only in water but also in acetone ?

10.24 Explain the significance of sodium, potassium, magnesium and calcium in biological fluids.

10.25 What happens when

(i) sodium metal is dropped in water ?

(ii) sodium metal is heated in free supply of air ?

(iii) sodium peroxide dissolves in water ?

10.26 Comment on each of the following observations:

(a) The mobilities of the alkali metal ions in aqueous solution are $Li^+ < Na^+ < K^+ < Rb^+ < Cs^+$

(b) Lithium is the only alkali metal to form a nitride directly.

(c) $\tilde{E}$ for $M^{2+}(aq) + 2e^- \rightarrow M(s)$ (where M = Ca, Sr or Ba) is nearly constant.

10.27 State as to why

(a) a solution of Na_2CO_3 is alkaline ?

(b) alkali metals are prepared by electrolysis of their fused chlorides ?

(c) sodium is found to be more useful than potassium ?

10.28 Write balanced equations for reactions between

(a) Na_2O_2 and water

(b) KO_2 and water

(c) Na_2O and CO_2.

10.29 How would you explain the following observations?

(i) BeO is almost insoluble but $BeSO_4$ is soluble in water,

(ii) BaO is soluble but $BaSO_4$ is insoluble in water,

(iii) LiI is more soluble than KI in ethanol.

10.30 Which of the alkali metal is having least melting point ?

(a) Na (b) K (c) Rb (d) Cs

10.31 Which one of the following alkali metals gives hydrated salts ?

(a) Li (b) Na (c) K (d) Cs

10.32 Which one of the alkaline earth metal carbonates is thermally the most stable ?

(a) $MgCO_3$ (b) $CaCO_3$ (c) $SrCO_3$ (d) $BaCO_3$

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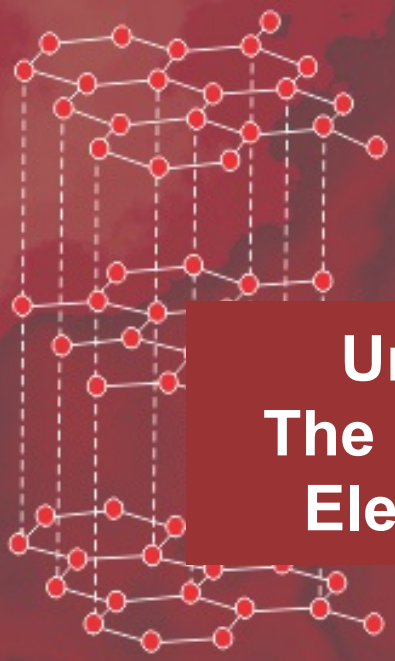
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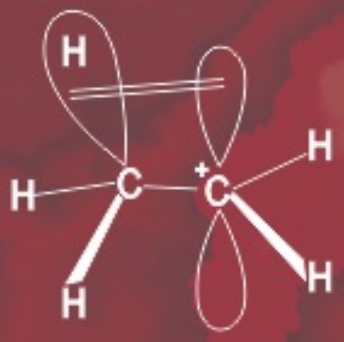
Textbook for Class XI



Unit 11
The p-Block Elements

Chemistry

Part II



11083CH11

Unit 11

The p -Block elements

Objectives

After studying this unit, you will be able to

• appreciate the general trends in the chemistry of p-block elements;

• describe the trends in physical and chemical properties of group 13 and 14 elements;

• explain anomalous behaviour of boron and carbon;

• describe allotropic forms of carbon;

• know the chemistry of some important compounds of boron, carbon and silicon;

• list the important uses of group 13 and 14 elements and their compounds.

"The variation in properties of the p-block elements due to the influence of d and f electrons in the inner core of the heavier

elements makes their chemistry interesting"

In p-block elements the last electron enters the outermost p orbital. As we know that the number of p orbitals is three and, therefore, the maximum number of electrons that can be accommodated in a set of p orbitals is six. Consequently there are six groups of p–block elements in the periodic table numbering from 13 to 18. Boron, carbon, nitrogen, oxygen, fluorine and helium head the groups. Their valence shell **electronic configuration is ns^2np^{1-6}**(except for He). The inner core of the electronic configuration may, however, differ. The difference in inner core of elements greatly influences their physical properties (such as atomic and ionic radii, ionisation enthalpy, etc.) as well as chemical properties. Consequently, a lot of variation in properties of elements in a group of p-block is observed. The maximum oxidation state shown by a p-block element is equal to the total number of valence electrons (i.e., the sum of the s- and p-electrons). Clearly, the number of possible oxidation states increases towards the right of the periodic table. In addition to this so called group oxidation state, p-block elements may show other oxidation states which normally, but not necessarily, differ from the total number of valence electrons by unit of two. The important oxidation states exhibited by p-block elements are shown in Table 11.1. In boron, carbon and nitrogen families the group oxidation state is the most stable state for the lighter elements in the group. However, the oxidation state two unit less than the group oxidation state becomes progressively more stable for the heavier elements in each group. The occurrence of oxidation states two unit less than the group oxidation states are sometime attributed to the 'inert pair effect'. The relative stabilities of these two oxidation states – group oxidation state and two unit less than the group oxidation state – may vary from group to group and will be

discussed at appropriate places.

Table 11.1 General Electronic Configuration and Oxidation States of p-Block Elements

Group	13	14	15	16	17	18
General electronic configuration	ns^2np^1	ns^2np^2	ns^2np^3	ns^2np^4	ns^2np^5	ns^2np^6 ($1s^2$ for He)
First member of the group	B	C	N	O	F	He
Group oxidation state	+3	+4	+5	+6	+7	+8
Other oxidation states	+1	+2, – 4	+3, – 3	+4, +2, –2	+5, + 3, +1, –1	+6, +4, +2

It is interesting to note that the non-metals and metalloids exist only in the p-block of the periodic table. The non-metallic character of elements decreases down the group. In fact the heaviest element in each p-block group is the most metallic in nature. This change from non-metallic to metallic character brings diversity in the chemistry of these elements depending on the group to which they belong.

In general, non-metals have higher ionisation enthalpies and higher electronegativities than the metals. Hence, in contrast to metals which readily form cations, non-metals readily form anions. The compounds formed by highly reactive non-metals with highly reactive metals are generally ionic because of large differences in their electronegativities. On the other hand, compounds formed between non-metals themselves are largely covalent in character because of small differences in their electronegativities. The change of non-metallic to metallic character can be best illustrated by the nature of oxides they form. The non-metal oxides are acidic or neutral whereas metal oxides are basic in nature.

The first member of p-block differs from the remaining members of their corresponding group in two major respects. First is the size and all other properties which depend on size. Thus, the lightest p-block elements show the same kind of differences as the lightest s-block elements, lithium and beryllium. The second important difference, which applies only to the p-block elements, arises from the effect of d-orbitals in the valence shell of heavier elements (starting from the third period onwards) and their lack in second period elements. The second period elements of p-groups starting from boron are restricted to a maximum covalence of four (using 2s and three 2p orbitals). In contrast, the third period elements of p-groups with the electronic configuration $3s^2 3p^n$ have the vacant 3d orbitals lying between the 3p and the 4s levels of energy. Using these d-orbitals the third period elements can expand their covalence above four. For example, while boron forms only $[BF_4]^-$, aluminium gives $[AlF_6]^{3-}$ ion. The presence of these d-orbitals influences the chemistry of the heavier elements in a number of other ways. The combined effect of size and availability of d orbitals considerably influences the ability of these elements to form π bonds. The first member of a group differs from the heavier members in its ability to form pπ - pπ multiple bonds to itself (e.g., C=C, C≡C, N≡N) and to other second row elements (e.g., C=O, C=N, C≡N, N=O). This type of π - bonding is not particularly strong for the heavier
p-block elements. The heavier elements do form π bonds but this involves d orbitals (dπ – pπ or dπ –dπ). As the d orbitals are of higher energy than the p orbitals, they contribute less to the overall stability of molecules than does pπ - pπ bonding of the second row elements. However, the coordination number in species of heavier elements may be higher than for the first element in the same oxidation state. For example,

in +5 oxidation state both N and P form oxoanions : NO^{3-} (three-coordination with π – bond involving one nitrogen p-orbital) and PO_4^{3-} (four-coordination involving s, p and d orbitals contributing to the π – bond). In this unit we will study the chemistry of group 13 and 14 elements of the periodic table.

11.1 GROUP 13 ELEMENTS: THE BORON FAMILY

This group elements show a wide variation in properties. Boron is a typical non-metal, aluminium is a metal but shows many chemical similarities to boron, and gallium, indium, thallium and nihonium are almost exclusively metallic in character.

Boron is a fairly rare element, mainly occurs as orthoboric acid, (H_3BO_3), borax, $Na_2B_4O_7 \cdot 10H_2O$, and kernite, $Na_2B_4O_7 \cdot 4H_2O$. In India borax occurs in Puga Valley (Ladakh) and Sambhar Lake (Rajasthan). The abundance of boron in earth crust is less than 0.0001% by mass. There are two isotopic forms of boron 10B (19%) and 11B (81%). Aluminium is the most abundant metal and the third most abundant element in the earth's crust (8.3% by mass) after oxygen (45.5%) and Si (27.7%). Bauxite, $Al_2O_3 . 2H_2O$ and cryolite, Na_3AlF_6 are the important minerals of aluminium. In India it is found as mica in Madhya Pradesh, Karnataka, Orissa and Jammu. Gallium, indium and thallium are less abundant elements in nature. Nihonium has symbol Nh, atomic number 113, atomic mass 286 g mol^{-1} and electronic configuration [Rn] $5f^{14}$ $6d^{10}$ $7s^2$ $7p^2$. So far it has been prepared in small amount and half life of its most stable isotope is 20 seconds. Due to these reasons its chemistry has not

been established.

Nihonium is a synthetically prepared radioactive element. Here atomic, physical and chemical properties of elements of this group leaving nihonium are discussed below.

11.1.1 Electronic Configuration

The outer electronic configuration of these elements is ns^2np^1. A close look at the electronic configuration suggests that while boron and aluminium have noble gas core, gallium and indium have noble gas plus 10 d-electrons, and thallium has noble gas plus 14 f- electrons plus 10 d-electron cores. Thus, the electronic structures of these elements are more complex than for the first two groups of elements discussed in unit 10. This difference in electronic structures affects the other properties and consequently the chemistry of all the elements of this group.

11.1.2 Atomic Radii

On moving down the group, for each successive member one extra shell of electrons is added and, therefore, atomic radius is expected to increase. However, a deviation can be seen. Atomic radius of Ga is less than that of Al. This can be understood from the variation in the inner core of the electronic configuration. The presence of additional 10 d-electrons offer only poor screening effect (Unit 2) for the outer electrons from the increased nuclear charge in gallium. Consequently, the atomic radius of gallium (135 pm) is less than that of aluminium (143 pm).

11.1.3 Ionization Enthalpy

The ionisation enthalpy values as expected from the general trends do

not decrease smoothly down the group. The decrease from B to Al is associated with increase in size. The observed discontinuity in the ionisation enthalpy values between Al and Ga, and between In and Tl are due to inability of d- and f-electrons ,which have low screening effect, to compensate the increase in nuclear charge.

The order of ionisation enthalpies, as expected, is $\Delta iH_1 < \Delta iH_2 < \Delta iH_3$. The sum of the first three ionisation enthalpies for each of the elements is very high. Effect of this will be apparent when you study their chemical properties.

11.1.4 Electronegativity

Down the group, electronegativity first decreases from B to Al and then increases marginally (Table 11.2). This is because of the discrepancies in atomic size of the elements.

11.1.5 Physical Properties

Boron is non-metallic in nature. It is extremely hard and black coloured solid. It exists in many allotropic forms. Due to very strong crystalline lattice, boron has unusually high melting point. Rest of the members are soft metals with low melting point and high electrical conductivity. It is worthwhile to note that gallium with unusually low melting point (303K), could exist in liquid state during summer. Its high boiling point (2676K) makes it a useful material for measuring high temperatures. Density of the elements increases down the group from boron to thallium.

11.1.6 Chemical Properties

Oxidation state and trends in chemical reactivity

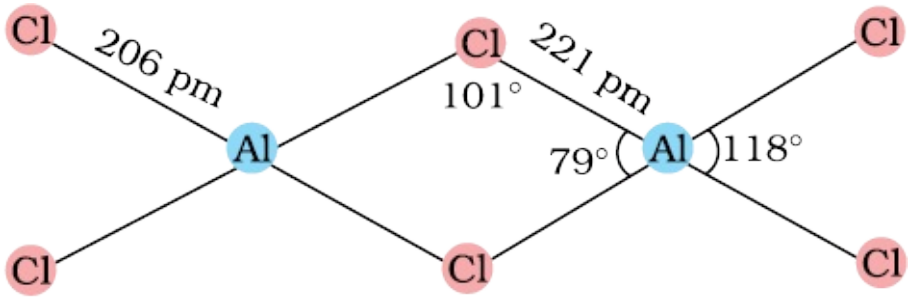
Due to small size of boron, the sum of its first three ionization enthalpies is very high. This prevents it to form +3 ions and forces it to form only covalent compounds. But as we move from B to Al, the sum of the first three ionisation enthalpies of Al considerably decreases, and is therefore able to form Al^{3+} ions. In fact, aluminium is a highly electropositive metal. However, down the group, due to poor shielding effect of intervening d and f orbitals, the increased effective nuclear charge holds ns electrons tightly (responsible for inert pair effect) and thereby, restricting their participation in bonding. As a result of this, only p-orbital electron may be involved in bonding. In fact in Ga, In and Tl, both +1 and +3 oxidation states are observed. The relative stability of +1 oxidation state progressively increases for heavier elements: Al<Ga<In<Tl. In thallium +1 oxidation state is predominant whereas the +3 oxidation state is highly oxidising in character. The compounds in +1 oxidation state, as expected from energy considerations, are more ionic than those in +3 oxidation state.

Table 11.2 Atomic and Physical Properties of Group 13 Elements

Property		Element				
		Boron B	Aluminium Al	Gallium Ga	Indium In	Thallium Tl
Atomic number		5	13	31	49	81
Atomic mass(g mol^{-1})		10.81	26.98	69.72	114.82	204.38
Electronic Configuration		$[He]2s^2 2p^1$	$[Ne]3s^2 3p^1$	$[Ar]3d^{10} 4s^2 4p^1$	$[Kr]4d^{10} 5s^2 5p^1$	$[Xe]4f^{14} 5d^{10} 6s^2 6p^1$
Atomic radius/pm[a]		(88)	143	135	167	170
Ionic radius M^{3+}/pm[b]		(27)	53.5	62.0	80.0	88.5
Ionic radius M^+/pm		-	-	120	140	150
Ionization enthalpy (kJ mol^{-1})	$\Delta_i H_1$	801	577	579	558	589
	$\Delta_i H_2$	2427	1816	1979	1820	1971
	$\Delta_i H_3$	3659	2744	2962	2704	2877
Electronegativity[c]		2.0	1.5	1.6	1.7	1.8
Density /g cm^{-3} at 298 K		2.35	2.70	5.90	7.31	11.85
Melting point / K		2453	933	303	430	576
Boiling point / K		3923	2740	2676	2353	1730
$E^\ominus$/ V for (M^{3+}/M)		-	–1.66	–0.56	–0.34	+1.26
$E^\ominus$ / V for (M^+/M)		-	+0.55	-0.79(acid) –1.39(alkali)	–0.18	–0.34

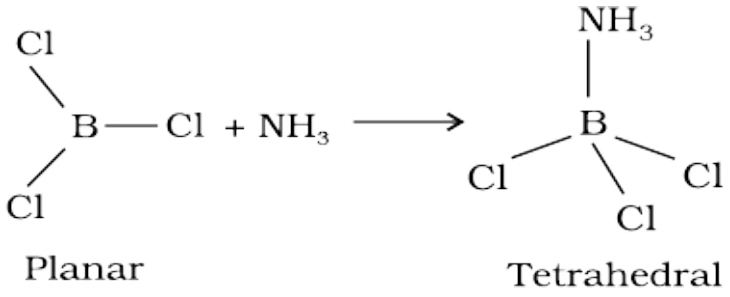
[a] *Metallic radius,* [b] *6-coordination,* [c] *Paulting scale,*

In trivalent state, the number of electrons around the central atom in a molecule of the compounds of these elements (e.g., boron in BF3) will be only six. Such electron deficient molecules have tendency to accept a pair of electrons to achieve stable electronic configuration and thus, behave as Lewis acids. The tendency to behave as Lewis acid decreases with the increase in the size down the group. BCl3 easily accepts a lone pair of electrons from ammonia to form BCl3·NH3.



Tetrahedral

$AlCl_3$ achieves stability by forming a dimer



In trivalent state most of the compounds being covalent are hydrolysed in water. For example, the trichlorides on hyrolysis in water form tetrahedral $\left[M(OH)_4\right]^-$ species; the hybridisation state of element M is sp^3. Aluminium chloride in acidified aqueous solution forms octahedral $\left[Al(H_2O)_6\right]^{3+}$ ion. In this complex ion, the 3d orbitals of Al are involved and the hybridisation state of Al is sp^3d^2.

Problem 11.1

Standard electrode potential values, $E^\ominus$ for Al^{3+}/Al is –1.66 V and that of Tl^{3+}/Tl is +1.26 V. Predict about the formation of M^{3+} ion in solution and compare the electropositive character of the two metals.

Solution

Standard electrode potential values for two half cell reactions suggest that aluminium has high tendency to make Al3+(aq) ions, whereas Tl^{3+} is not only unstable in solution but is a powerful oxidising agent also. Thus Tl^+ is more stable in solution than Tl^{3+}. Aluminium being able to form +3 ions easily, is more electropositive than thallium.

(i) Reactivity towards air

Boron is unreactive in crystalline form. Aluminium forms a very thin oxide layer on the surface which protects the metal from further attack. Amorphous boron and aluminium metal on heating in air form B2O3 and Al2O3 respectively. With dinitrogen at high temperature they form nitrides.

$$2E(s) + 3O_2(g) \xrightarrow{\Delta} 2E_2O_3(s)$$

$$2E(s) + N_2(g) \xrightarrow{\Delta} 2EN(s)$$

(E = element)

The nature of these oxides varies down the group. Boron trioxide is acidic and reacts with basic (metallic) oxides forming metal borates. Aluminium and gallium oxides are amphoteric and those of indium and thallium are basic in their properties.

(ii) Reactivity towards acids and alkalies

Boron does not react with acids and alkalies even at moderate temperature; but aluminium dissolves in mineral acids and aqueous alkalies and thus shows amphoteric character.

Aluminium dissolves in dilute HCl and liberates dihydrogen.

$2Al(s) + 6HCl(aq) \rightarrow 2Al_3+(aq) + 6Cl–(aq) + 3H_2(g)$

However, concentrated nitric acid renders aluminium passive by forming a protective oxide layer on the surface.

Aluminium also reacts with aqueous alkali and liberates dihydrogen.

2Al (s) + 2NaOH(aq) + 6H2O(l)

↓

2 Na+ [Al(OH)4] –(aq) + 3H2(g)

Sodium

tetrahydroxoaluminate(III)

(iii) Reactivity towards halogens

These elements react with halogens to form trihalides (except TlI3).

$2E(s) + 3\ X_2\ (g) \rightarrow 2EX_3\ (s)$ (X = F, Cl, Br, I)

Problem 11.2

White fumes appear around the bottle of anhydrous aluminium chloride. Give reason.

Solution

Anhydrous aluminium chloride is partially hydrolysed with atmospheric moisture to liberate HCl gas. Moist HCl appears white in colour.

11.2 IMPORTANT TRENDS AND ANOMALOUS PROPERTIES OF BORON

Certain important trends can be observed in the chemical behaviour of group 13 elements. The tri-chlorides, bromides and iodides of all these elements being covalent in nature are hydrolysed in water. Species like tetrahedral $[M(OH)_4]^-$ and octahedral $[M(H_2O)_6]^{3+}$, except in boron, exist in aqueous medium.

The monomeric trihalides, being electron deficient, are strong Lewis acids. Boron trifluoride easily reacts with Lewis bases such as NH3 to complete octet around boron.

$$F_3B + :NH_3 \rightarrow F_3B \leftarrow NH_3$$

It is due to the absence of d orbitals that the maximum covalence of B is 4. Since the d orbitals are available with Al and other elements, the maximum covalence can be expected beyond 4. Most of the other metal halides (e.g., $AlCl_3$) are dimerised through halogen bridging (e.g., Al_2Cl_6). The metal species completes its octet by accepting electrons from halogen in these halogen bridged molecules.

Problem 11.3

Boron is unable to form BF63– ion. Explain.

Solution

Due to non-availability of d orbitals, boron is unable to expand its octet. Therefore, the maximum covalence of boron cannot exceed 4.

11.3 SOME IMPORTANT COMPOUNDS OF BORON

Some useful compounds of boron are borax, orthoboric acid and diborane. We will briefly study their chemistry.

11.3.1 Borax

It is the most important compound of boron. It is a white crystalline solid of formula $Na_2B_4O_7 \cdot 10H_2O$. In fact it contains the tetranuclear units $\left[B_4O_5(OH)_4\right]^{2-}$ and correct formula; therefore, is $Na_2[B_4O_5$ (OH)4].$8H_2O$. Borax dissolves in water to give an alkaline solution.

$$Na_2B_4O_7 + 7H_2O \rightarrow 2NaOH + 4H_3BO_3$$

Orthoboric acid

On heating, borax first loses water molecules and swells up. On further heating it turns into a transparent liquid, which solidifies into glass like material known as borax bead.

$$Na2B4O7.10H2O \xrightarrow{\Delta} Na2B4O7 \xrightarrow{\Delta} 2NaBO2 + B_2O_3$$

Sodium metaborate Boric anhydride

The metaborates of many transition metals have characteristic colours and, therefore, borax bead test can be used to identify them in the laboratory. For example, when borax is heated in a Bunsen burner flame with CoO on a loop of platinum wire, a blue coloured $Co(BO_2)_2$ bead is formed.

11.3.2 Orthoboric acid

Orthoboric acid, H_3BO_3 is a white crystalline solid, with soapy touch. It is sparingly soluble in water but highly soluble in hot water. It can be prepared by acidifying an aqueous solution of borax.

$$Na_2B_4O_7 + 2HCl + 5H_2O \rightarrow 2NaCl + 4B(OH)_3$$

It is also formed by the hydrolysis (reaction with water or dilute acid) of most boron compounds (halides, hydrides, etc.). It has a layer structure in which planar BO3 units are joined by hydrogen bonds as shown in Fig. 11.1.

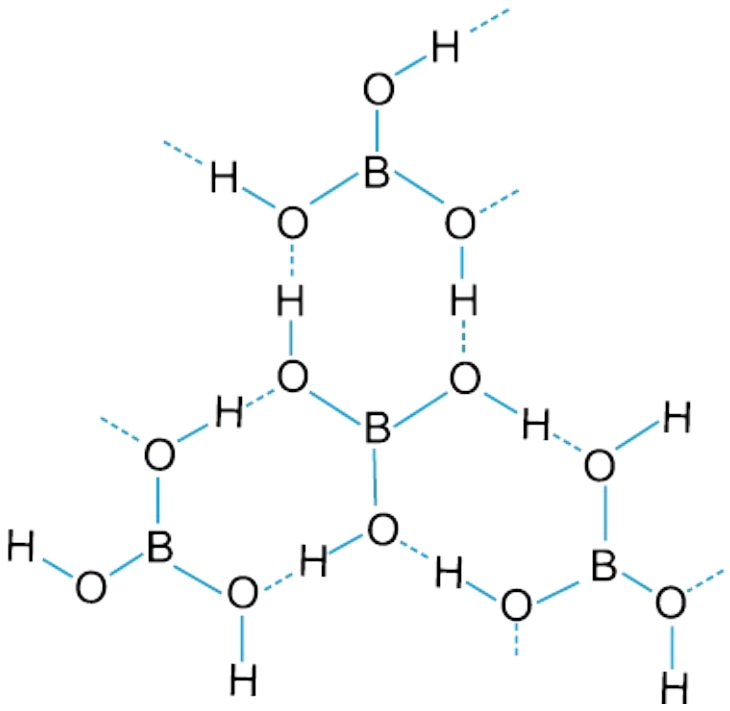


Fig. 11. 1 Structure of boric acid; the dotted lines represent hydrogen bonds

Boric acid is a weak monobasic acid. It is not a protonic acid but acts as a Lewis acid by accepting electrons from a hydroxyl ion:

$$B(OH)_3 + 2HOH \rightarrow [B(OH)_4]^- + H3O^+$$

On heating, orthoboric acid above 370K forms metaboric acid, HBO2 which on further heating yields boric oxide, B2O3.

$$H_3BO_3 \xrightarrow{\Delta} HBO_2 \xrightarrow{\Delta} B_2O_3$$

Problem 11.4

Why is boric acid considered as a weak acid?

Solution

Because it is not able to release H+ ions on its own. It receives OH^- ions from water molecule to complete its octet and in turn releases H^+ ions.

11.3.3 Diborane, B2H6

The simplest boron hydride known, is diborane. It is prepared by treating boron trifluoride with $LiAlH_4$ in diethyl ether.

$$4BF_3 + 3\ LiAlH_4 \rightarrow 2B_2H_6 + 3LiF + 3AlF_3$$

A convenient laboratory method for the preparation of diborane involves the oxidation of sodium borohydride with iodine.

$$2NaBH_4 + I_2 \rightarrow B_2H_6 + 2NaI + H_2$$

Diborane is produced on an industrial scale by the reaction of BF_3 with sodium hydride.

$$2BF_3 + 6NaH \xrightarrow{450K} B_2H_6 + 6NaF$$

Diborane is a colourless, highly toxic gas with a b.p. of 180 K. Diborane catches fire spontaneously upon exposure to air. It burns in oxygen releasing an enormous amount of energy.

$$B_2H_6 + 3O_2 \rightarrow B_2O_3 + 3H_2O;$$
$$\Delta_c H^{\ominus} = -1976\ kJ\ mol^{-1}$$

Most of the higher boranes are also spontaneously flammable in air. Boranes are readily hydrolysed by water to give boric acid.

$$B_2H_6(g) + 6H_2O(l) \rightarrow 2B(OH)_3(aq) + 6H_2(g)$$

Diborane undergoes cleavage reactions with Lewis bases(L) to give borane adducts, BH3·L

$$B_2H_6 + 2\ NMe_3 \rightarrow 2BH_3{\cdot}NMe_3$$

$$B_2H_6 + 2\ CO \rightarrow 2BH_3{\cdot}CO$$

Reaction of ammonia with diborane gives initially $B_2H6.2NH_3$ which is formulated as $[BH_2(NH_3)_2]^+$ $[BH_4]^-$; further heating gives borazine, $B_3N_3H_6$ known as “inorganic benzene” in view of its ring structure with alternate BH and NH groups.

$$3B_2H_6 + 6NH_3 \rightarrow 3[BH_2(NH_3)_2]^+[BH_4]^- \xrightarrow{\text{Heat}} 2B_3N_3H_6 + 12H_2$$

The structure of diborane is shown in Fig.11.2(a). The four terminal hydrogen atoms and the two boron atoms lie in one plane. Above and below this plane, there are two bridging hydrogen atoms. The four terminal B-H bonds are regular two centre-two electron bonds while the two bridge (B-H-B) bonds are different and can be described in terms of three centre–two electron bonds shown in Fig.11.2 (b).

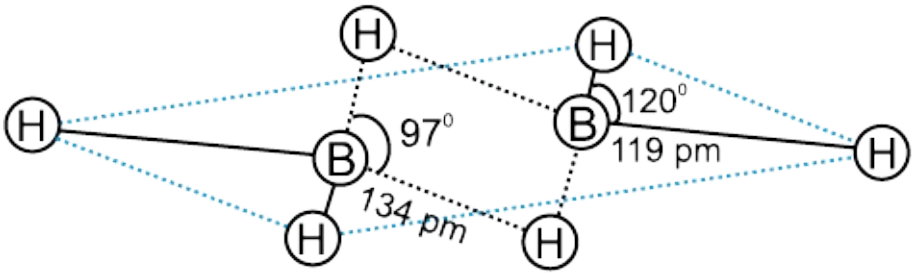


Fig.11.2(a) The structure of diborane, B_2H_6

Boron also forms a series of hydridoborates; the most important one is the tetrahedral $[BH_4]^-$ ion. Tetrahydridoborates of several metals are known. Lithium and sodium tetra-hydridoborates, also known as **borohydrides**, are prepared by the reaction of metal hydrides with B2H6 in diethyl ether.

$2MH + B_2H_6 \rightarrow 2\ M^+\ [BH_4]^-$ (M = Li or Na)

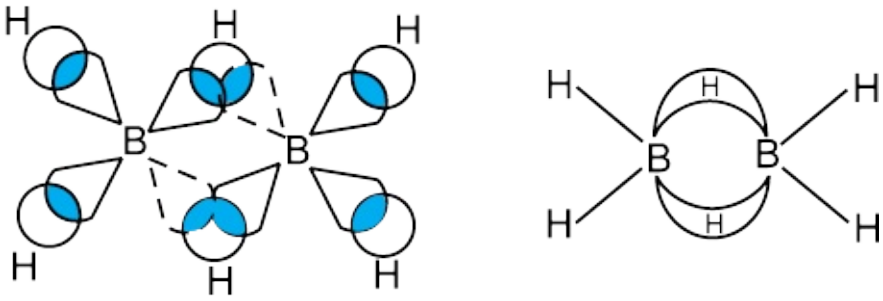


Fig.11.2(b) Bonding in diborane. Each B atom uses sp3 hybrids for bonding. Out of the four sp3 hybrids on each B atom, one is without an electron shown in broken lines. The terminal B-H bonds are normal 2-centre-2-electron bonds but the two bridge bonds are 3-centre-2-electron bonds. The 3-centre-2-electron bridge bonds are also referred to as banana bonds.

Both $LiBH_4$ and $NaBH_4$ are used as reducing agents in organic synthesis. They are useful starting materials for preparing other metal borohydrides.

11.4 USES OF BORON AND ALUMINIUM AND THEIR COMPOUNDS

Boron being extremely hard refractory solid of high melting point, low density and very low electrical conductivity, finds many applications. Boron fibres are used in making bullet-proof vest and light composite material for aircraft. The boron-10 (10B) isotope has high ability to absorb neutrons and, therefore, metal borides are used in nuclear industry as protective shields and control rods. The main industrial application of borax and boric acid is in the manufacture of heat resistant glasses (e.g., Pyrex), glass-wool and fibreglass. Borax is also used as a flux for soldering metals, for heat, scratch and stain resistant glazed coating to earthenwares and as constituent of medicinal soaps. An aqueous solution of orthoboric acid is generally used as a mild antiseptic.

Aluminium is a bright silvery-white metal, with high tensile strength. It has a high electrical and thermal conductivity. On a weight-to-weight basis,

the electrical conductivity of aluminium is twice that of copper. Aluminium is used extensively in industry and everyday life. It forms alloys with Cu, Mn, Mg, Si and Zn. Aluminium and its alloys can be given shapes of pipe, tubes, rods, wires, plates or foils and, therefore, find uses in packing, utensil making, construction, aeroplane and transportation industry. The use of aluminium and its compounds for domestic purposes is now reduced considerably because of their toxic nature.

11.5 GROUP 14 ELEMENTS: THE CARBON FAMILY

Carbon, silicon, germanium, tin lead and flerovium are the members of group 14. Carbon is the seventeenth most abundant element by mass in the earth's crust. It is widely distributed in nature in free as well as in the combined state. In elemental state it is available as coal, graphite and diamond; however, in combined state it is present as metal carbonates, hydrocarbons and carbon dioxide gas (0.03%) in air. One can emphatically say that carbon is the most versatile element in the world. Its combination with other elements such as dihydrogen, dioxygen, chlorine and sulphur provides an astonishing array of materials ranging from living tissues to drugs and plastics. Organic chemistry is devoted to carbon containing compounds. It is an essential constituent of all living organisms. Naturally occurring carbon contains two stable isotopes:12C and 13C. In addition to these, third isotope, 14C is also present. It is a radioactive isotope with half-life 5770 years and used for radiocarbon dating. Silicon is the second (27.7 % by mass) most abundant element on the earth's crust and is present in nature in the form of silica and silicates. Silicon is a very important component of ceramics, glass and cement. Germanium exists only in traces. Tin occurs mainly as cassiterite, SnO_2 and lead as galena, PbS. Flerovium is synthetically

prepared radioactive element

Ultrapure form of germanium and silicon are used to make transistors and semiconductor devices.

Symbol of Flerovium is Fl. It has atomic number 114, atomic mass 289 $gmol^{-1}$ and electronic configuration [Rn] $5f^{14}6d^{10}$ $7s^2$ $7p^2$. It has been prepared only in small amount. Its half life is short and its chemistry has not been established yet. The important atomic and physical properties along with their electronic configuration of the elements of group 14 leaving flerovium are given in Table 11.3. Some of the atomic, physical and chemical properties are discussed below:

11.5.1 Electronic Configuration

The valence shell electronic configuration of these elements is ns^2np^2. The inner core of the electronic configuration of elements in this group also differs.

11.5.2 Covalent Radius

There is a considerable increase in covalent radius from C to Si, thereafter from Si to Pb a small increase in radius is observed. This is due to the presence of completely filled d and f orbitals in heavier members.

Table 11.3 Atomic and Physical Properties of Group 14 Elements

Property		Element				
		Carbon C	Silicon Si	Germanium Ge	Tin Sn	Lead Pb
Atomic Number		6	14	32	50	82
Atomic mass (g mol^{-1})		12.01	28.09	72.60	118.71	207.2
Electronic configuration		$[He]2s^2 2p^2$	$[Ne]3s^2 3p^2$	$[Ar]3d^{10} 4s^2 4p^2$	$[Kr]4d^{10} 5s^2 5p^2$	$[Xe]4f^{14} 5d^{10} 6s^2 6p^2$
Covalent radius/pm[a]		77	118	122	140	146
Ionic radius M^{4+}/pm[b]		–	40	53	69	78
Ionic radius M^{2+}/pm[b]		–	–	73	118	119
Ionization enthalpy/ kJ mol^{-1}	$\Delta_i H_1$	1086	786	761	708	715
	$\Delta_i H_2$	2352	1577	1537	1411	1450
	$\Delta_i H_3$	4620	3228	3300	2942	3081
	$\Delta_i H_4$	6220	4354	4409	3929	4082
Electronegativity[c]		2.5	1.8	1.8	1.8	1.9
Density[d]/g cm^{-3}		3.51[e]	2.34	5.32	7.26[f]	11.34
Melting point/K		4373	1693	1218	505	600
Boiling point/K		–	3550	3123	2896	2024
Electrical resistivity/ ohm cm (293 K)		10^{14}–10^{16}	50	50	10^{-5}	2×10^{-5}

[a]for M^{IV} oxidation state; [b] 6–coordination; [c] Pauling scale; [d] 293 K; [e] for diamond; for graphite, density is 2.22; [f]β-form (stable at room temperature)

11.5.3 Ionization Enthalpy

The first ionization enthalpy of group 14 members is higher than the corresponding members of group 13. The influence of inner core electrons is visible here also. In general the ionisation enthalpy decreases down the group. Small decrease in $\Delta_i H$ from Si to Ge to Sn and slight increase in $\Delta_i H$ from Sn to Pb is the consequence of poor shielding effect of intervening d and f orbitals and increase in size of the atom.

11.5.4 Electronegativity

Due to small size, the elements of this group are slightly more electronegative than group 13 elements. The electronegativity values for elements from Si to Pb are almost the same.

11.5.5 Physical Properties

All members of group14 are solids. Carbon and silicon are non-metals, germanium is a metalloid, whereas tin and lead are soft metals with low melting points. Melting points and boiling points of group 14 elements are much higher than those of corresponding elements of group 13.

11.5.6 Chemical Properties

Oxidation states and trends in chemical reactivity

The group 14 elements have four electrons in outermost shell. The common oxidation states exhibited by these elements are +4 and +2. Carbon also exhibits negative oxidation states. Since the sum of the first four ionization enthalpies is very high, compounds in +4 oxidation state are generally covalent in nature. In heavier members the tendency to show +2 oxidation state increases in the sequence Ge<Sn<Pb. It is due to the inability of ns^2 electrons of valence shell to participate in bonding. The relative stabilities of these two oxidation states vary down the group. Carbon and silicon mostly show +4 oxidation state. Germanium forms stable compounds in +4 state and only few compounds in +2 state. Tin forms compounds in both oxidation states (Sn in +2 state is a reducing agent). Lead compounds in +2 state are stable and in +4 state are strong oxidising agents. In tetravalent state the number of electrons around the central atom in a molecule (e.g., carbon in CCl_4) is eight. Being electron precise molecules, they are normally not expected to act as electron

acceptor or electron donor species. Although carbon cannot exceed its covalence more than 4, other elements of the group can do so. It is because of the presence of d orbital in them. Due to this, their halides undergo hydrolysis and have tendency to form complexes by accepting electron pairs from donor species. For example, the species like, SiF_6^{2-}, $[GeCl_6]^{2-}$, $[Sn(OH)_6]^{2-}$ exist where the hybridisation of the central atom is sp^3d^2.

(i) Reactivity towards oxygen

All members when heated in oxygen form oxides. There are mainly two types of oxides, i.e., monoxide and dioxide of formula MO and MO_2 respectively. SiO only exists at high temperature. Oxides in higher oxidation states of elements are generally more acidic than those in lower oxidation states. The dioxides — CO_2, SiO_2 and GeO_2 are acidic, whereas SnO_2 and PbO_2 are amphoteric in nature. Among monoxides, CO is neutral, GeO is distinctly acidic whereas SnO and PbO are amphoteric.

Problem 11.5

Select the member(s) of group 14 that
(i) forms the most acidic dioxide, (ii) is commonly found in +2 oxidation state,
(iii) used as semiconductor.

Solution

(i) carbon (ii) lead

(iii) silicon and germanium

(ii) Reactivity towards water

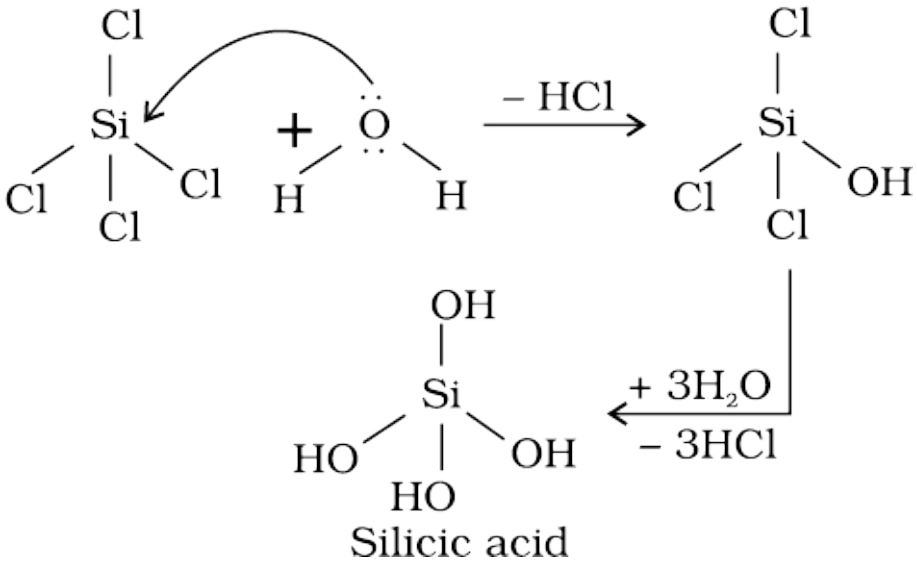
Carbon, silicon and germanium are not affected by water. Tin decomposes steam to form dioxide and dihydrogen gas.

$$Sn + 2H_2O \xrightarrow{\Delta} SnO_2 + 2H_2$$

Lead is unaffected by water, probably because of a protective oxide film formation.

(iii) Reactivity towards halogen

These elements can form halides of formula MX_2 and MX_4 (where X = F, Cl, Br, I). Except carbon, all other members react directly with halogen under suitable condition to make halides. Most of the MX_4 are covalent in nature. The central metal atom in these halides undergoes sp3 hybridisation and the molecule is tetrahedral in shape. Exceptions are SnF_4 and PbF_4, which are ionic in nature. PbI_4 does not exist because Pb—I bond initially formed during the reaction does not release enough energy to unpair $6s^2$ electrons and excite one of them to higher orbital to have four unpaired electrons around lead atom. Heavier members Ge to Pb are able to make halides of formula MX_2. Stability of dihalides increases down the group. Considering the thermal and chemical stability, GeX_4 is more stable than GeX_2, whereas PbX_2 is more than PbX_4. Except CCl_4, other tetrachlorides are easily hydrolysed by water because the central atom can accommodate the lone pair of electrons from oxygen atom of water molecule in d orbital.



Hydrolysis can be understood by taking the example of $SiCl_4$. It undergoes hydrolysis by initially accepting lone pair of electrons from water molecule in d orbitals of Si, finally leading to the formation of $Si(OH)_4$ as shown below :

Problem 11. 6

$[SiF_6]^{2-}$ is known whereas $[SiCl_6]^{2-}$ not. Give possible reasons.

Solution

The main reasons are :

(i) six large chloride ions cannot be accommodated around Si^{4+} due to limitation of its size.

(ii) interaction between lone pair of chloride ion and Si^{4+} is not very strong.

11.6 IMPORTANT TRENDS AND ANOMALOUS

BEHAVIOUR OF CARBON

Like first member of other groups, carbon also differs from rest of the members of its group. It is due to its smaller size, higher electronegativity, higher ionisation enthalpy and unavailability of d orbitals.

In carbon, only s and p orbitals are available for bonding and, therefore, it can accommodate only four pairs of electrons around it. This would limit the maximum covalence to four whereas other members can expand their covalence due to the presence of d orbitals.

Carbon also has unique ability to form pπ– pπ multiple bonds with itself and with other atoms of small size and high electronegativity. Few examples of multiple bonding are: C=C, C ≡ C, C = O, C = S, and C ≡ N. Heavier elements do not form pπ– pπ bonds because their atomic orbitals are too large and diffuse to have effective overlapping.

Carbon atoms have the tendency to link with one another through covalent bonds to form chains and rings. This property is called **catenation**. This is because C—C bonds are very strong. Down the group the size increases and electronegativity decreases, and, thereby, tendency to show catenation decreases. This can be clearly seen from bond enthalpies values. The order of catenation is C > > Si > Ge ≈ Sn. Lead does not show catenation.

Bond	Bond enthalpy / kJ mol $^{-1}$
C—C	348
Si —Si	297
Ge—Ge	260
Sn—Sn	240

Due to property of catenation and pπ– pπ bond formation, carbon is able to show allotropic forms.

11.7 ALLOTROPES OF CARBON

Carbon exhibits many allotropic forms; both crystalline as well as amorphous. Diamond and graphite are two well-known crystalline forms of carbon. In 1985, third form of carbon known as fullerenes was discovered by H.W.Kroto, E.Smalley and R.F.Curl. For this discovery they were awarded the Nobel Prize in 1996.

11.7.1 Diamond

It has a crystalline lattice. In diamond each carbon atom undergoes sp3 hybridisation and linked to four other carbon atoms by using hybridised orbitals in tetrahedral fashion. The C–C bond length is 154 pm. The structure extends in space and produces a rigid three-dimensional network of carbon atoms. In this structure (Fig. 11.3) directional covalent bonds are present throughout the lattice.

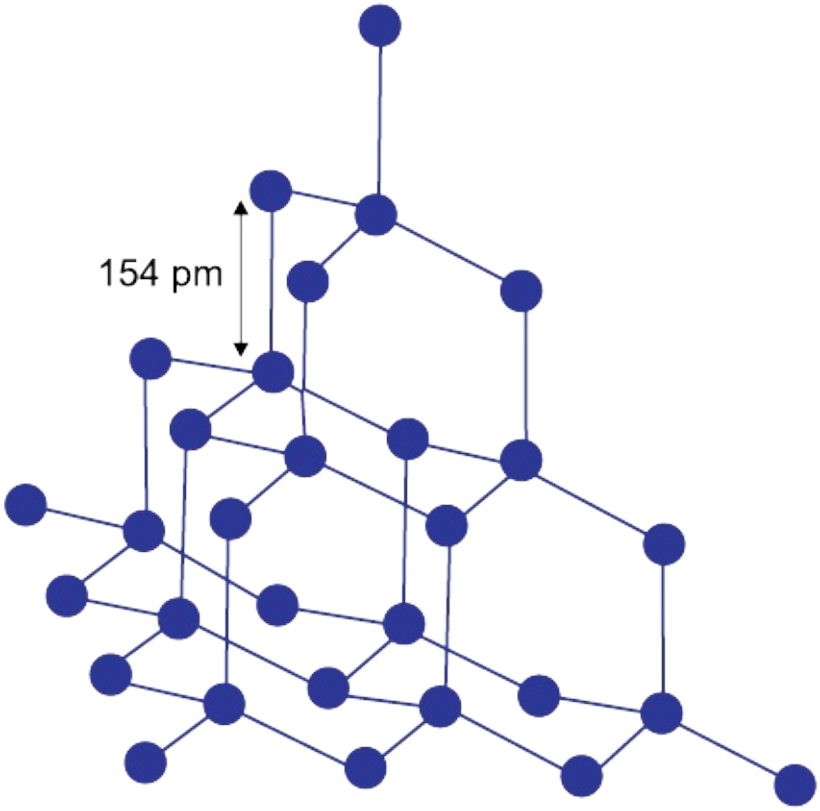


Fig. 11.3 The structure of diamond

It is very difficult to break extended covalent bonding and, therefore, diamond is a hardest substance on the earth. It is used as an abrasive for sharpening hard tools, in making dyes and in the manufacture of tungsten filaments for electric light bulbs.

Problem 11.7

Diamond is covalent, yet it has high melting point. Why ?

Solution

Diamond has a three-dimensional network involving strong C—C bonds, which are very difficult to break and, in turn has high melting point.

11.7.2 Graphite

Graphite has layered structure (Fig.11.4). Layers are held by van der Waals forces and distance between two layers is 340 pm. Each layer is composed of planar hexagonal rings of carbon atoms. C—C bond length within the layer is 141.5 pm. Each carbon atom in hexagonal ring undergoes sp2 hybridisation and makes three sigma bonds with three neighbouring carbon atoms. Fourth electron forms a π bond. The electrons are delocalised over the whole sheet. Electrons are mobile and, therefore, graphite conducts electricity along the sheet. Graphite cleaves easily between the layers and, therefore, it is very soft and slippery. For this reason graphite is used as a dry lubricant in machines running at high temperature, where oil cannot be used as a lubricant.

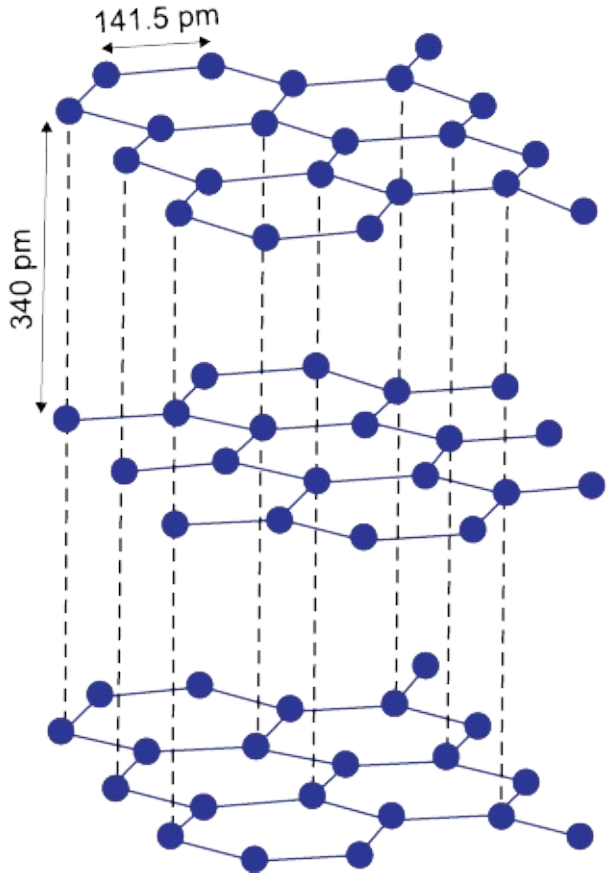


Fig 11.4 The structure of graphite

11.7.3 Fullerenes

Fullerenes are made by the heating of graphite in an electric arc in the presence of inert gases such as helium or argon. The sooty material formed by condensation of vapourised Cn small molecules consists of mainly C60 with smaller quantity of C70 and traces of fullerenes consisting of even number of carbon atoms up to 350 or above. Fullerenes are the only pure form of carbon because they have smooth structure without having 'dangling' bonds. Fullerenes are cage like molecules. C60 molecule has a shape like soccer ball and called **Buckminsterfullerene** (Fig. 11.5).

It contains twenty six- membered rings and twelve five-membered rings. A six membered ring is fused with six or five membered rings but a five membered ring can only fuse with six membered rings. All the carbon atoms are equal and they undergo sp2 hybridisation. Each carbon atom forms three sigma bonds with other three carbon atoms. The remaining electron at each carbon is delocalised in molecular orbitals, which in turn give aromatic character to molecule. This ball shaped molecule has 60 vertices and each one is occupied by one carbon atom and it also contains both single and double bonds with C–C distances of 143.5 pm and 138.3 pm respectively. Spherical fullerenes are also called bucky ballsin short.

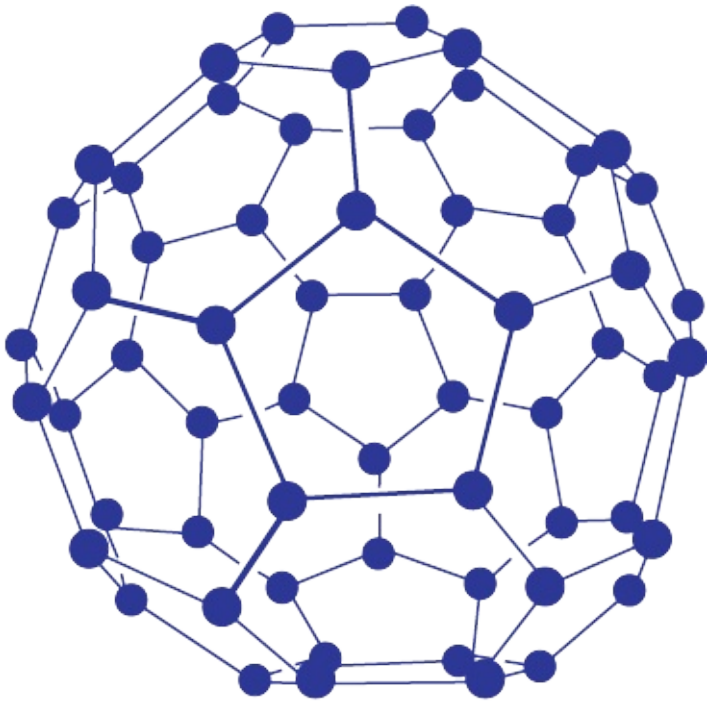


Fig.11.5 The structure of C60, Buckminster-fullerene : Note that molecule has the shape of a soccer ball (football).

It is very important to know that graphite is thermodynamically most stable allotrope of carbon and, therefore, $\Delta f H^{\circ}$ of graphite is taken as

zero. $\Delta f H^{\ominus}$ values of diamond and fullerene, C60 are 1.90 and 38.1 kJ mol^{-1}, respectively.

Other forms of elemental carbon like carbon black, coke, and charcoal are all impure forms of graphite or fullerenes. Carbon black is obtained by burning hydrocarbons in a limited supply of air. Charcoal and coke are obtained by heating wood or coal respectively at high temperatures in the absence of air.

11.7.4 Uses of Carbon

Graphite fibres embedded in plastic material form high strength, lightweight composites. The composites are used in products such as tennis rackets, fishing rods, aircrafts and canoes. Being good conductor, graphite is used for electrodes in batteries and industrial electrolysis. Crucibles made from graphite are inert to dilute acids and alkalies. Being highly porous, activated charcoal is used in adsorbing poisonous gases; also used in water filters to remove organic contaminators and in airconditioning system to control odour. Carbon black is used as black pigment in black ink and as filler in automobile tyres. Coke is used as a fuel and largely as a reducing agent in metallurgy. Diamond is a precious stone and used in jewellery. It is measured in carats (1 carat = 200 mg).

11.8 SOME IMPORTANT COMPOUNDS OF CARBON AND SILICON

Oxides of Carbon

Two important oxides of carbon are carbon monoxide, CO and carbon dioxide, CO_2.

11.8.1 Carbon Monoxide

Direct oxidation of C in limited supply of oxygen or air yields carbon monoxide.

$$2C(s) + O_2(g) \xrightarrow{\Delta} 2CO(g)$$

On small scale pure CO is prepared by dehydration of formic acid with concentrated H_2SO_4 at 373 K

$$HCOOH \xrightarrow[\text{conc.}H_2SO_4]{373K} H_2O + CO$$

On commercial scale it is prepared by the passage of steam over hot coke. The mixture of CO and H2 thus produced is known as **water gas** or **synthesis gas**.

$$C(s) + H_2O(g) \xrightarrow{473-1273K} \underset{\text{Water gas}}{CO(g) + H_2(g)}$$

When air is used instead of steam, a mixture of CO and N_2 is produced, which is called **producer gas**.

$$2C(s) + O_2(g) + 4N_2(g) \xrightarrow{1273K} \underset{\text{Producer gas}}{2CO(g) + 4N_2(g)}$$

Water gas and producer gas are very important industrial fuels. Carbon monoxide in water gas or producer gas can undergo further combustion forming carbon dioxide with the liberation of heat.

Carbon monoxide is a colourless, odourless and almost water insoluble gas. It is a powerful reducing agent and reduces almost all metal oxides other than those of the alkali and alkaline earth metals, aluminium and a few transition metals. This property of CO is used in the extraction of

many metals from their oxides ores.

$$Fe_2O_3(s) + 3CO(g) \xrightarrow{\Delta} 2Fe(s) + 3CO_2(g)$$

$$ZnO(s) + CO(g) \xrightarrow{\Delta} Zn(s) + CO_2(g)$$

In CO molecule, there are one sigma and two π bonds between carbon and oxygen, :C ≡ O: . Because of the presence of a lone pair on carbon, CO molecule acts as a donor and reacts with certain metals when heated to form metal carbonyls. The highly poisonous nature of CO arises because of its ability to form a complex with haemoglobin, which is about 300 times more stable than the oxygen-haemoglobin complex. This prevents haemoglobin in the red blood corpuscles from carrying oxygen round the body and ultimately resulting in death.

11.8.2 Carbon Dioxide

It is prepared by complete combustion of carbon and carbon containing fuels in excess of air.

$$C(s) + O_2(g) \xrightarrow{\Delta} CO_2(g)$$

$$CH_4(g) + 2O_2(g) \xrightarrow{\Delta} CO_2(g) + 2H_2O(g)$$

In the laboratory it is conveniently prepared by the action of dilute HCl on calcium carbonate.

$$CaCO_3(s) + 2HCl\ (aq) \rightarrow CaCl_2\ (aq) + CO_2\ (g) + H_2O(l)$$

On commercial scale it is obtained by heating limestone.

It is a colourless and odourless gas. Its low solubility in water makes it of immense bio-chemical and geo-chemical importance. With water, it forms carbonic acid, H_2CO_3 which is a weak dibasic acid and dissociates in two steps:

$$H_2CO_3(aq) + H_2O(l) \quad HCO_3^-(aq) + H_3O+(aq)$$

$$HCO_3^- (aq) + H_2O(l) \; CO32– (aq) + H_3O+(aq)$$

H_2CO_3/HCO_3^- buffer system helps to maintain pH of blood between 7.26 to 7.42. Being acidic in nature, it combines with alkalies to form metal carbonates.

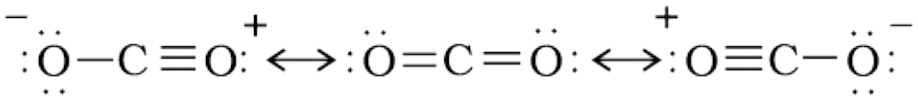
Carbon dioxide, which is normally present to the extent of ~ 0.03 % by volume in the atmosphere, is removed from it by the process known as photosynthesis. It is the process by which green plants convert atmospheric CO_2 into carbohydrates such as glucose. The overall chemical change can be expressed as:

$$6CO_2 + 12H_2O \xrightarrow[\text{Chlorophyll}]{h\nu} C_6H_{12}O_6 + 6O_2 + 6H_2O$$

By this process plants make food for themselves as well as for animals and human beings. Unlike CO, it is not poisonous. But the increase in combustion of fossil fuels and decomposition of limestone for cement manufacture in recent years seem to increase the CO_2 content of the atmosphere. This may lead to increase in **green house effect** and thus, raise the temperature of the atmosphere which might have serious consequences.

Carbon dioxide can be obtained as a solid in the form of **dry ice** by allowing the liquified CO_2 to expand rapidly. Dry ice is used as a refrigerant for ice-cream and frozen food. Gaseous CO_2 is extensively used to carbonate soft drinks. Being heavy and non-supporter of combustion it is used as fire extinguisher. A substantial amount of CO_2 is used to manufacture urea.

In CO_2 molecule carbon atom undergoes sp hybridisation. Two sp hybridised orbitals of carbon atom overlap with two p orbitals of oxygen atoms to make two sigma bonds while other two electrons of carbon atom are involved in pπ– pπ bonding with oxygen atom. This results in its linear shape [with both C–O bonds of equal length (115 pm)] with no dipole moment. The resonance structures are shown below:



Resonance structures of carbon dioxide

11.8.3 Silicon Dioxide, SiO2

95% of the earth's crust is made up of silica and silicates. Silicon dioxide, commonly known as silica, occurs in several crystallographic forms. Quartz, cristobalite and tridymite are some of the crystalline forms of silica, and they are interconvertable at suitable temperature. Silicon dioxide is a covalent, three-dimensional network solid in which each silicon atom is covalently bonded in a tetrahedral manner to four oxygen atoms. Each oxygen atom in turn covalently bonded to another silicon atoms as shown in diagram (Fig 11.6). Each corner is shared with another tetrahedron. The entire crystal may be considered as giant molecule in which eight membered rings are formed with alternate silicon and oxygen atoms.

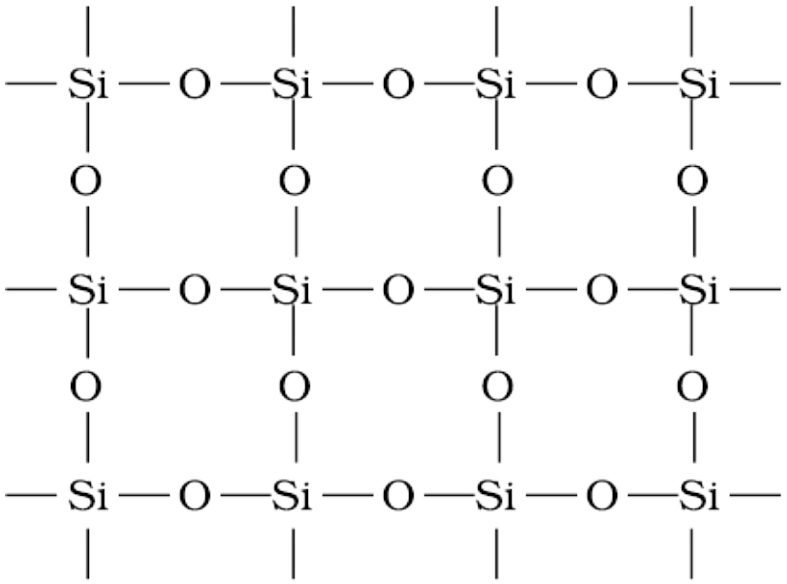


Fig. 11.6 Three dimensional structure of SiO2

Silica in its normal form is almost non-reactive because of very high Si —O bond enthalpy. It resists the attack by halogens, dihydrogen and most of the acids and metals even at elevated temperatures. However, it is attacked by HF and NaOH.

$$SiO_2 + 2NaOH \rightarrow Na_2SiO_3 + H_2O$$

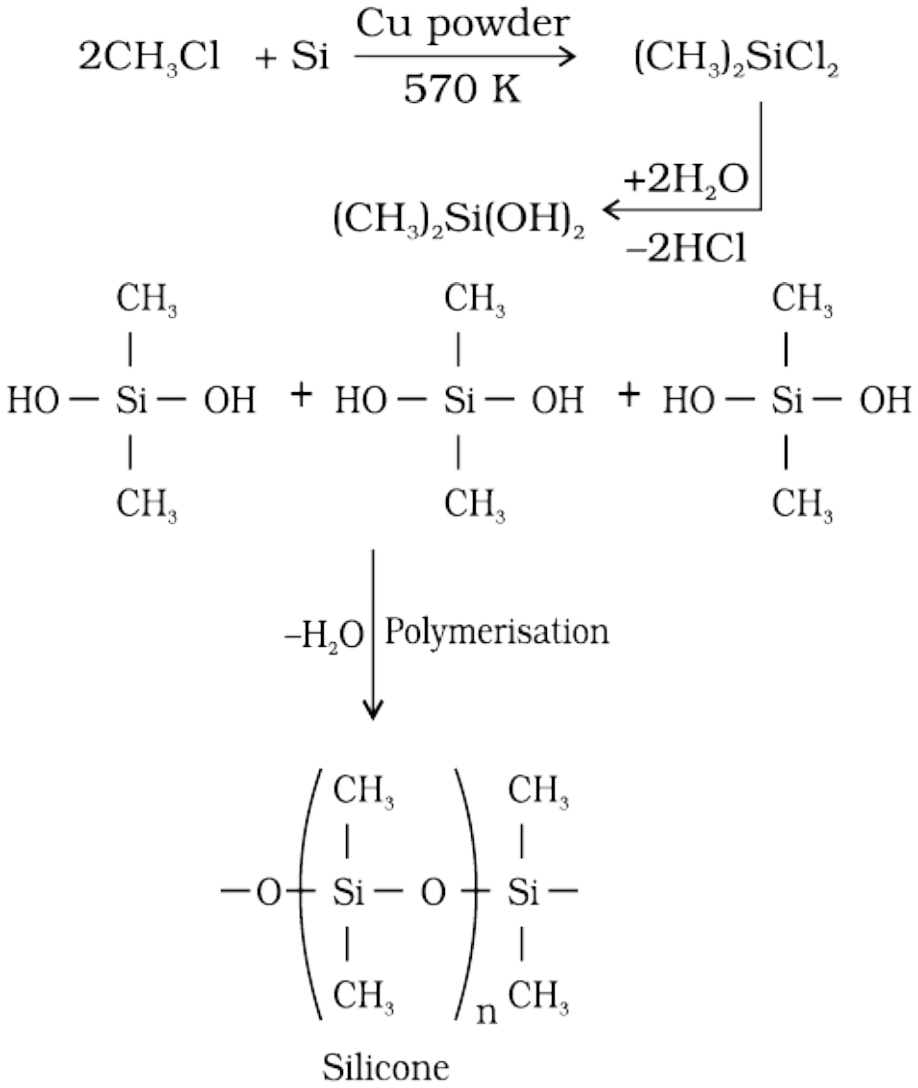
$$SiO_2 + 4HF \rightarrow SiF_4 + 2H_2O$$

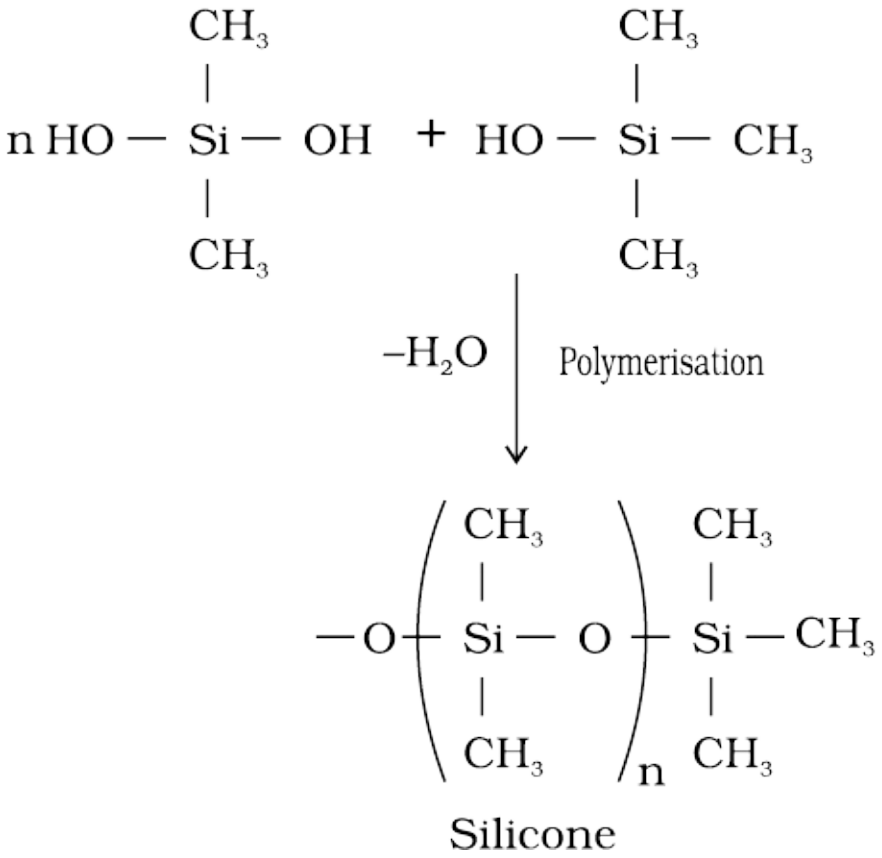
Quartz is extensively used as a piezoelectric material; it has made possible to develop extremely accurate clocks, modern radio and television broadcasting and mobile radio communications. Silica gel is used as a drying agent and as a support for chromatographic materials and catalysts. Kieselghur, an amorphous form of silica is used in filtration plants.

11.8.4 Silicones

They are a group of organosilicon polymers, which have (R_2SiO) as a

repeating unit. The starting materials for the manufacture of silicones are alkyl or aryl substituted silicon chlorides, $R_nSiCl_{(4-n)}$, where R is alkyl or aryl group. When methyl chloride reacts with silicon in the presence of copper as a catalyst at a temperature 573K various types of methyl substituted chlorosilane of formula $MeSiCl_3$, Me_2SiCl_2, Me_3SiCl with small amount of Me_4Si are formed. Hydrolysis of dimethyl-dichlorosilane, $(CH_3)_2SiCl_2$ followed by condensation polymerisation yields straight chain polymers.





Silicone

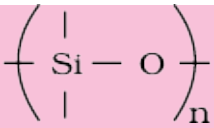
The chain length of the polymer can be controlled by adding $(CH_3)_3SiCl$ which blocks the ends as shown below :

Silicones being surrounded by non-polar alkyl groups are water repelling in nature. They have in general high thermal stability, high dielectric strength and resistance to oxidation and chemicals. They have wide applications. They are used as sealant, greases, electrical insulators and for water proofing of fabrics. Being biocompatible they are also used in surgical and cosmetic plants.

Problem: 11.8

What are silicones ?

Solution

Simple silicones consist of  chains in which alkyl or phenyl groups occupy the remaining bonding positions on each silicon. They are hydrophobic (water repellant) in nature.

11.8.5 Silicates

A large number of silicates minerals exist in nature. Some of the examples are feldspar, zeolites, mica and asbestos. The basic structural unit of silicates is SiO_4^{4-} (Fig.11.7) in which silicon atom is bonded to four oxygen atoms in tetrahedron fashion. In silicates either the discrete unit is present or a number of such units are joined together via corners by sharing 1,2,3 or 4 oxygen atoms per silicate units. When silicate units are linked together, they form chain, ring, sheet or three-dimensional structures. Negative charge on silicate structure is neutralised by positively charged metal ions. If all the four corners are shared with other tetrahedral units, three-dimensional network is formed.

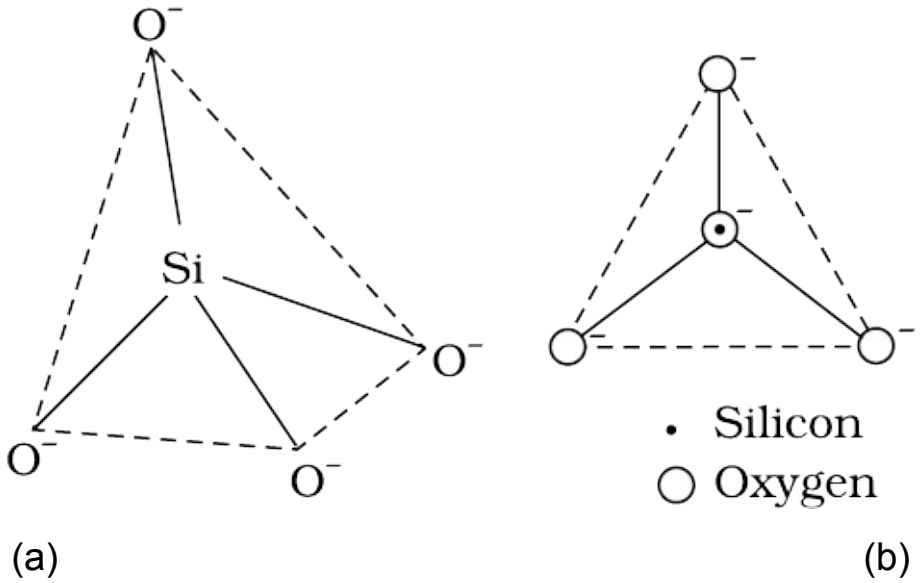


Fig. 11.7 (a) Tetrahedral structure of SiO44–anion; (b) Representation of SiO44–unit

Two important man-made silicates are glass and cement.

11.8.6 Zeolites

If aluminium atoms replace few silicon atoms in three-dimensional network of silicon dioxide, overall structure known as aluminosilicate, acquires a negative charge. Cations such as Na^+, K^+ or Ca^{2+} balance the negative charge. Examples are feldspar and zeolites. Zeolites are widely used as a catalyst in petrochemical industries for cracking of hydrocarbons and isomerisation, e.g., ZSM-5 (A type of zeolite) used to convert alcohols directly into gasoline. Hydrated zeolites are used as ion exchangers in softening of “hard” water.

SUMMARY

p-Block of the periodic table is unique in terms of having all types of elements – **metals**, **non-metals** and **metalloids**. There are six groups of p-block elements in the periodic table numbering from 13 to 18. Their valence shell electronic configuration is $ns^2np^{1–6}$ (except for He). Differences in the **inner core** of their electronic configuration greatly influence their physical and chemical properties. As a consequence of this, a lot of variation in properties among these elements is observed. In addition to the group oxidation state, these elements show other oxidation states differing from the total number of valence electrons by unit of two. While the group oxidation state is the most stable for the lighter elements of the group, lower oxidation states become progressively more stable for the heavier elements. The combined effect of size and availability of d orbitals considerably influences the ability of these elements to form π-bonds. While the lighter elements form **pπ–pπ** bonds, the heavier ones form **dπ–pπ** or **dπ–dπ** bonds. Absence of d orbital in second period elements limits their maximum covalence to 4 while heavier ones can exceed this limit.

Boron is a typical non-metal and the other members are metals. The availability of 3 valence electrons ($2s^2 2p^1$) for covalent bond formation using four orbitals (2s, $2p_x$, $2p_y$ and $2p_z$) leads to the so called **electron deficiency** in boron compounds. This deficiency makes them good electron acceptor and thus boron compounds behave as **Lewis acids**. Boron forms covalent molecular compounds with dihydrogen as boranes, the simplest of which is **diborane**, B_2H_6. Diborane contains two bridging hydrogen atoms between two boron atoms; these bridge bonds are considered to be **three-centre two-electron bonds**. The important compounds of boron with dioxygen are **boric acid** and **borax**. Boric acid, $B(OH)_3$ is a weak monobasic acid; it acts as a Lewis acid by accepting electrons from hydroxyl ion. Borax is a white crystalline solid of formula $Na_2[B_4O_5(OH)_4]\cdot 8H_2O$. The borax bead test gives characteristic colours of transition metals.

Aluminium exhibits +3 oxidation state. With heavier elements +1 oxidation state gets progressively stabilised on going down the group. This is a consequence of the so called **inert pair effect**.

Carbon is a typical non-metal forming covalent bonds employing all its four valence electrons ($2s^2 2p^2$). It shows the property of **catenation**, the ability to form chains or rings, not only with C–C single bonds but also with multiple bonds (C=C or C≡C). The tendency to catenation decreases as C>>Si>Ge ~ Sn > Pb. Carbon provides one of the best examples of allotropy. Three important allotropes of carbon are **diamond**, **graphite** and **fullerenes**. The members of the carbon family mainly exhibit +4 and +2 oxidation states; compouds in +4 oxidation states are generally covalent in nature. The tendency to show +2 oxidation state increases among heavier elements. Lead in +2 state is stable whereas in +4 oxidation state it is a strong oxidising agent. Carbon also exhibits negative oxidation states. It forms two important oxides: CO and CO_2. Carbon monoxide is neutral whereas CO_2 is acidic in nature. Carbon monoxide having lone pair of electrons on C forms metal carbonyls. It is deadly poisonous due to higher stability of its haemoglobin

complex as compared to that of oxyhaemoglobin complex. Carbon dioxide as such is not toxic. However, increased content of CO_2 in atmosphere due to combustion of fossil fuels and decomposition of limestone is feared to cause increase in 'green house effect'. This, in turn, raises the temperature of the atmosphere and causes serious complications. Silica, silicates and silicones are important class of compounds and find applications in industry and technology.

EXERCISES

11.1 Discuss the pattern of variation in the oxidation states of

(i) B to Tl and (ii) C to Pb.

11.2 How can you explain higher stability of BCl_3 as compared to $TlCl_3$?

11.3 Why does boron triflouride behave as a Lewis acid ?

11.4 Consider the compounds, BCl_3 and CCl_4. How will they behave with
water ? Justify.

11.5 Is boric acid a protic acid ? Explain.

11.6 Explain what happens when boric acid is heated .

11.7 Describe the shapes of BF_3 and BH_4^-. Assign the hybridisation of boron in these species.

11.8 Write reactions to justify amphoteric nature of aluminium.

11.9 What are electron deficient compounds ? Are BCl_3 and $SiCl_4$ electron deficient species ? Explain.

11.10 Write the resonance structures of $CO_3^{2-}$and HCO_3^- .

11.11 What is the state of hybridisation of carbon in (a) CO_3^{2-} (b) diamond

(c) graphite?

11.12 Explain the difference in properties of diamond and graphite on the basis of their structures.

11.13 Rationalise the given statements and give chemical reactions :

• Lead(II) chloride reacts with Cl_2 to give $PbCl_4$.

• Lead(IV) chloride is highly unstable towards heat.

• Lead is known not to form an iodide, PbI_4.

11.14 Suggest reasons why the B–F bond lengths in BF_3 (130 pm) and BF_4^-
(143 pm) differ.

11.15 If B–Cl bond has a dipole moment, explain why BCl_3 molecule has zero dipole moment.

11.16 Aluminium trifluoride is insoluble in anhydrous HF but dissolves on addition of NaF. Aluminium trifluoride precipitates out of the resulting solution when gaseous BF_3 is bubbled through. Give reasons.

11.17 Suggest a reason as to why CO is poisonous.

11.18 How is excessive content of CO_2 responsible for global warming ?

11.19 Explain structures of diborane and boric acid.

11.20 What happens when

(a) Borax is heated strongly,

(b) Boric acid is added to water,

(c) Aluminium is treated with dilute NaOH,

(d) BF_3 is reacted with ammonia ?

11.21 Explain the following reactions

(a) Silicon is heated with methyl chloride at high temperature in the presence of copper;

(b) Silicon dioxide is treated with hydrogen fluoride;

(c) CO is heated with ZnO;

(d) Hydrated alumina is treated with aqueous NaOH solution.

11.22 Give reasons :

(i) Conc. HNO_3 can be transported in aluminium container.

(ii) A mixture of dilute NaOH and aluminium pieces is used to open drain.

(iii) Graphite is used as lubricant.

(iv) Diamond is used as an abrasive.

(v) Aluminium alloys are used to make aircraft body.

(vi) Aluminium utensils should not be kept in water overnight.

(vii) Aluminium wire is used to make transmission cables.

11.23 Explain why is there a phenomenal decrease in ionization enthalpy from carbon to silicon ?

11.24 How would you explain the lower atomic radius of Ga as compared to Al ?

11.25 What are allotropes? Sketch the structure of two allotropes of carbon namely diamond and graphite. What is the impact of structure on physical properties of two allotropes?

11.26 (a) Classify following oxides as neutral, acidic, basic or amphoteric:

CO, B_2O_3, SiO_2, CO_2, Al_2O_3, PbO_2, Tl_2O_3

(b) Write suitable chemical equations to show their nature.

11.27 In some of the reactions thallium resembles aluminium, whereas in others it resembles with group I metals. Support this statement by giving some evidences.

11.28 When metal X is treated with sodium hydroxide, a white precipitate (A) is obtained, which is soluble in excess of NaOH to give soluble complex (B). Compound (A) is soluble in dilute HCl to form

compound (C). The compound (A) when heated strongly gives (D), which is used to extract metal. Identify (X), (A), (B), (C) and (D). Write suitable equations to support their identities.

11.29 What do you understand by (a) inert pair effect (b) allotropy and (c) catenation?

11.30 A certain salt X, gives the following results.

(i) Its aqueous solution is alkaline to litmus.

(ii) It swells up to a glassy material Y on strong heating.

(iii) When conc. H_2SO_4 is added to a hot solution of X,white crystal of an acid Z separates out.

Write equations for all the above reactions and identify X, Y and Z.

11.31 Write balanced equations for:

(i) $BF_3 + LiH \rightarrow$

(ii) $B_2H_6 + H_2O \rightarrow$

(iii) $NaH + B_2H_6 \rightarrow$

(iv) $H_3BO_3 \xrightarrow{\Delta}$

(v) $Al + NaOH \rightarrow$

(vi) $B_2H_6 + NH_3 \rightarrow$

11.32. Give one method for industrial preparation and one for laboratory preparation of CO and CO_2 each.

11.33 An aqueous solution of borax is

(a) neutral (b) amphoteric

(c) basic (d) acidic

11.34 Boric acid is polymeric due to

(a) its acidic nature (b) the presence of hydrogen bonds

(c) its monobasic nature (d) its geometry

11.35 The type of hybridisation of boron in diborane is

(a) sp (b) sp^2 (c) sp^3 (d) dsp^2

11.36 Thermodynamically the most stable form of carbon is

(a) diamond (b) graphite

(c) fullerenes (d) coal

11.37 Elements of group 14

(a) exhibit oxidation state of +4 only

(b) exhibit oxidation state of +2 and +4

(c) form M^{2-} and M^{4+} ions

(d) form M^{2+} and M^{4+} ions

11.38 If the starting material for the manufacture of silicones is $RSiCl_3$, write the structure of the product formed.

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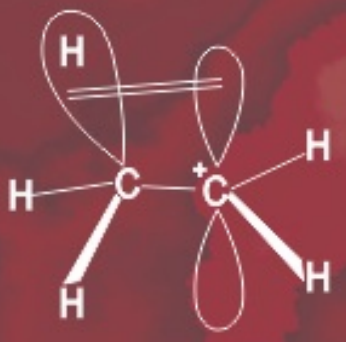
Textbook for Class XI



Unit 12
Organic Chemistry – Some Basic Principles and Techniques

Chemistry

Part II



11083CH12

UNIT 12

Organic Chemistry – Some Basic Principles and Techniques

Objectives

After studying this unit, you will be able to

• understand reasons for tetravalence of carbon and shapes of organic molecules;

• write structures of organic molecules in various ways;

• classify the organic compounds;

• name the compounds according to IUPAC system of nomenclature and also derive their structures from the given names;

• understand the concept of organic reaction mechanism;

• explain the influence of electronic displacements on structure and reactivity of organic compounds;

• recognise the types of organic reactions;

• learn the techniques of purification of organic compounds;

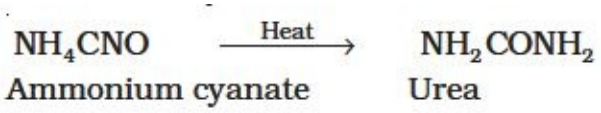
- write the chemical reactions involved in the qualitative analysis of organic compounds;
- understand the principles involved in quantitative analysis of organic compounds.

In the previous unit you have learnt that the element carbon has the unique property called catenation due to which it forms covalent bonds with other carbon atoms. It also forms covalent bonds with atoms of other elements like hydrogen, oxygen, nitrogen, sulphur, phosphorus and halogens. The resulting compounds are studied under a separate branch of chemistry called **organic chemistry**. This unit incorporates some basic principles and techniques of analysis required for understanding the formation and properties of organic compounds.

12.1 GENERAL INTRODUCTION

Organic compounds are vital for sustaining life on earth and include complex molecules like genetic information bearing deoxyribonucleic acid (DNA) and proteins that constitute essential compounds of our blood, muscles and skin. Organic compounds appear in materials like clothing, fuels, polymers, dyes and medicines. These are some of the important areas of application of these compounds.

Science of organic chemistry is about two hundred years old. Around the year 1780, chemists began to distinguish between organic compounds obtained from plants and animals and inorganic compounds prepared from mineral sources. Berzilius, a Swedish chemist proposed that a ‘vital force’ was responsible for the formation of organic compounds. However, this notion was rejected in 1828 when F. Wohler synthesised an organic compound, urea from an inorganic compound, ammonium cyanate.



The pioneering synthesis of acetic acid by Kolbe (1845) and that of methane by Berthelot (1856) showed conclusively that organic compounds could be synthesised from inorganic sources in a laboratory.

The development of electronic theory of covalent bonding ushered organic chemistry into its modern shape.

12.2 TETRAVALENCE OF CARBON: SHAPES OF ORGANIC COMPOUNDS

12.2.1 The Shapes of Carbon Compounds

The knowledge of fundamental concepts of molecular structure helps in understanding and predicting the properties of organic compounds. You have already learnt theories of valency and molecular structure in Unit 4. Also, you already know that tetravalence of carbon and the formation of covalent bonds by it are explained in terms of its electronic configuration and the hybridisation of s and p orbitals. It may be recalled that formation and the shapes of molecules like methane (CH_4), ethene (C_2H_4), ethyne (C_2H_2) are explained in terms of the use of sp3, sp2 and sp hybrid orbitals by carbon atoms in the respective molecules.

Hybridisation influences the bond length and bond enthalpy (strength) in compounds. The sp hybrid orbital contains more s character and hence it is closer to its nucleus and forms shorter and stronger bonds than the sp3 hybrid orbital. The sp^2 hybrid orbital is intermediate in s character between sp and sp3 and, hence, the length and enthalpy of the bonds it forms, are also intermediate between them. The change in hybridisation

affects the electronegativity of carbon. The greater the s character of the hybrid orbitals, the greater is the electronegativity. Thus, a carbon atom having an sp hybrid orbital with 50% s character is more electronegative than that possessing sp^2 or sp^3 hybridised orbitals. This relative electronegativity is reflected in several physical and chemical properties of the molecules concerned, about which you will learn in later units.

12.2.2 Some Characteristic Features of π Bonds

In a π (pi) bond formation, parallel orientation of the two p orbitals on adjacent atoms is necessary for a proper sideways overlap. Thus, in $H_2C=CH_2$ molecule all the atoms must be in the same plane. The p orbitals are mutually parallel and both the p orbitals are perpendicular to the plane of the molecule. Rotation of one CH_2 fragment with respect to other interferes with maximum overlap of p orbitals and, therefore, such rotation about carbon-carbon double bond (C=C) is restricted. The electron charge cloud of the π bond is located above and below the plane of bonding atoms. This results in the electrons being easily available to the attacking reagents. In general, π bonds provide the most reactive centres in the molecules containing multiple bonds.

Problem 12.1

How many σ and π bonds are present in each of the following molecules?

(a) $HC\equiv CCH=CHCH_3$ (b) $CH_2=C=CHCH_3$

Solution

(a) σ_{C-C}: 4; σ_{C-H} : 6; $\pi_{C=C}$:1; $\pi_{C\equiv C}$:2

(b) σ_{C-C}: 3; σ_{C-H}: 6; $\pi_{C=C}$: 2.

Problem 12.2

What is the type of hybridisation of each carbon in the following compounds?

(a) CH_3Cl, (b) $(CH_3)_2CO$, (c) CH_3CN,

(d) $HCONH_2$, (e) $CH_3CH=CHCN$

Solution

(a) sp^3, (b) sp^3, sp^2, (c) sp^3, sp, (d) sp^2, (e) sp^3, sp^2, sp^2, sp

Problem 12.3

Write the state of hybridisation of carbon in the following compounds and shapes of each of the molecules.

(a) $H_2C=O$, (b) CH_3F, (c) $HC\equiv N$.

Solution

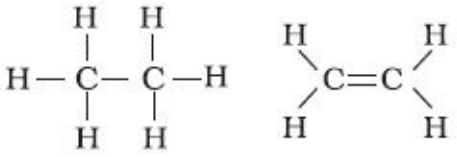
(a) sp^2 hybridised carbon, trigonal planar; (b) sp^3 hybridised carbon, tetrahedral; (c) sp hybridised carbon, linear.

12.3 STRUCTURAL REPRESENTATIONS OF ORGANIC COMPOUNDS

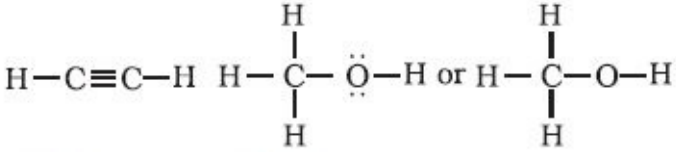
12.3.1 Complete, Condensed and Bond-line Structural Formulas

Structures of organic compounds are represented in several ways. The Lewis structure or dot structure, dash structure, condensed structure and bond line structural formulas are some of the specific types. The Lewis structures, however, can be simplified by representing the two-electron covalent bond by a dash (–). Such a structural formula focuses on the electrons involved in bond formation. A single dash represents a single

bond, double dash is used for double bond and a triple dash represents triple bond. Lone-pairs of electrons on heteroatoms (e.g., oxygen, nitrogen, sulphur, halogens etc.) may or may not be shown. Thus, ethane (C_2H_6), ethene (C_2H_4), ethyne (C_2H_2) and methanol (CH_3OH) can be represented by the following structural formulas. Such structural representations are called complete structural formulas.



Ethane *Ethene*



Ethyne *Methanol*

These structural formulas can be further abbreviated by omitting some or all of the dashes representing covalent bonds and by indicating the number of identical groups attached to an atom by a subscript. The resulting expression of the compound is called a condensed structural formula. Thus, ethane, ethene, ethyne and methanol can be written as:

CH_3CH_3	$H_2C=CH_2$	$HC\equiv CH$	CH_3OH
Ethane	Ethene	Ethyne	Methanol

Similarly, $CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_3$ can be further condensed to $CH_3(CH_2)_6CH_3$. For further simplification, organic chemists use another way of representing the structures, in which only lines are used. In this bond-line structural representation of organic compounds, carbon and hydrogen atoms are not shown and the lines representing carbon-carbon bonds are drawn in a zig-zag fashion. The only atoms specifically

written are oxygen, chlorine, nitrogen etc. The terminals denote methyl (–CH_3) groups (unless indicated otherwise by a functional group), while the line junctions denote carbon atoms bonded to appropriate number of hydrogens required to satisfy the valency of the carbon atoms. Some of the examples are represented as follows:

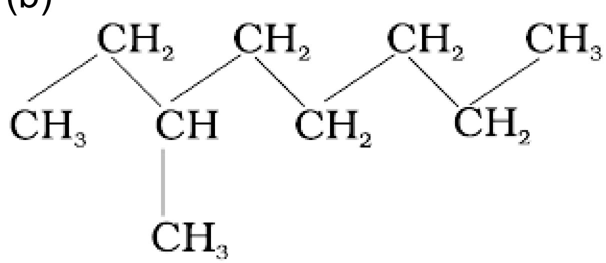
(i) 3-Methyloctane can be represented in various forms as:

(a) CH_3 CH_2 $CHCH_2$ CH_2 CH_2 CH_2 CH_3

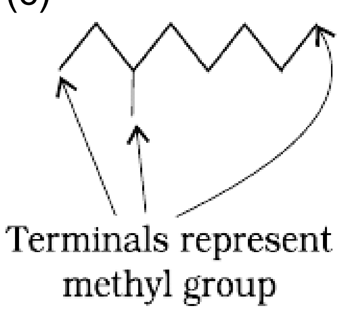
|

CH_3

(b)



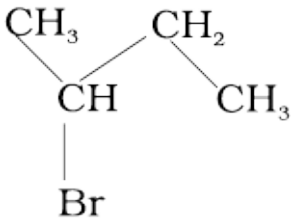
(c)



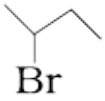
(ii) Various ways of representing 2-bromo butane are:

(a) CH3CHBrCH2CH3

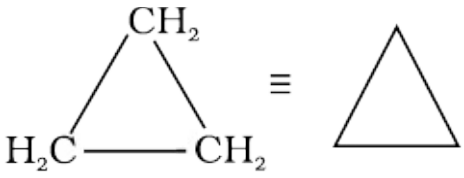
(b)



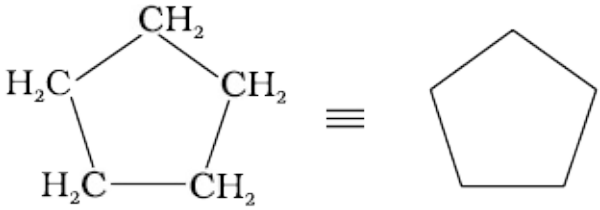
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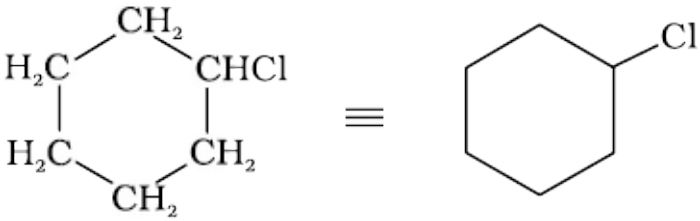
In cyclic compounds, the bond-line formulas may be given as follows:



Cyclopropane



Cyclopentane



chlorocyclohexane

Problem 12.4

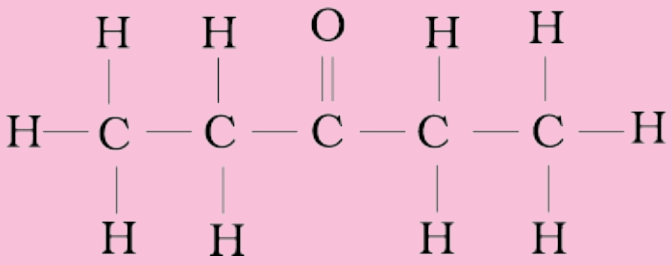
Expand each of the following condensed formulas into their complete structural formulas.

(a) $CH_3CH_2COCH_2CH_3$

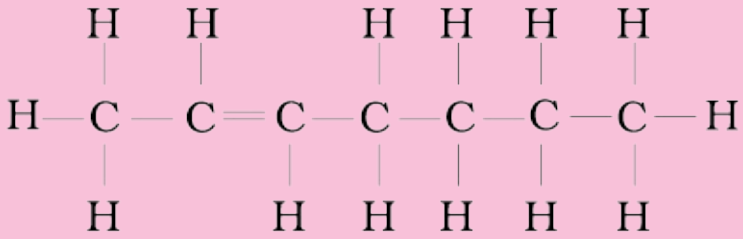
(b) $CH_3CH{=}CH(CH_2)_3CH_3$

Solution

(a)



(b)

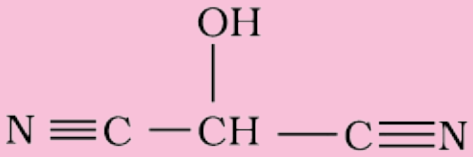


Problem 12.5

For each of the following compounds, write a condensed formula and also their bond-line formula.

(a) $HOCH_2CH_2CH_2CH(CH_3)CH(CH_3)CH_3$

(b)



Solution

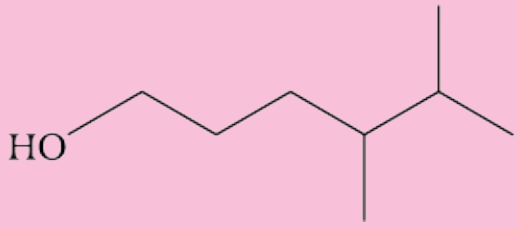
Condensed formula:

(a) $HO(CH_2)_3CH(CH_3)CH(CH_3)_2$

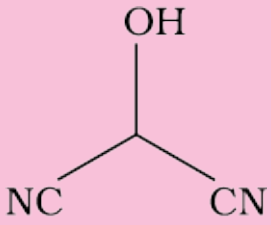
(b) $HOCH(CN)_2$

Bond-line formula:

(a)



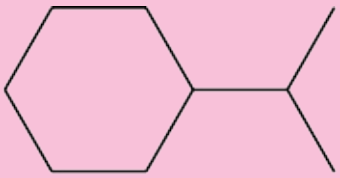
(b)



Problem 12.6

Expand each of the following bond-line formulas to show all the atoms including carbon and hydrogen

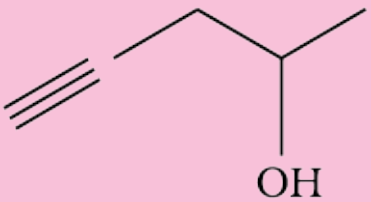
(a)



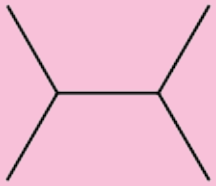
(b)



(c)

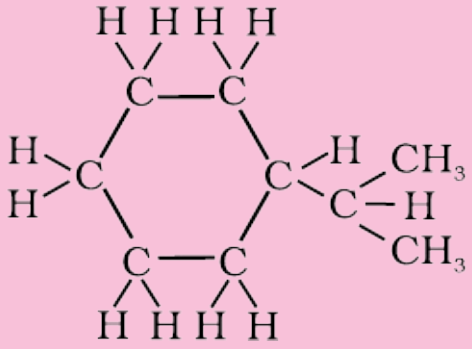


(d)

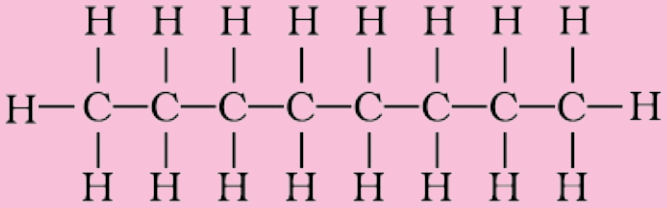


Solution

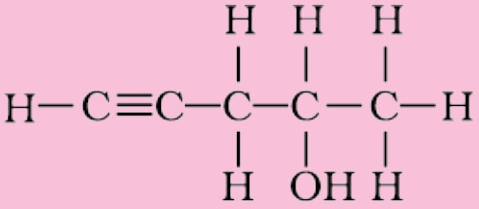
(a)



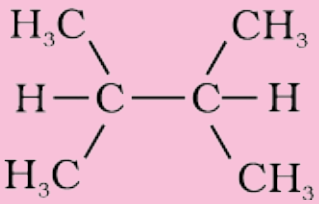
(b)



(c)



(d)



12.3.2 Three-Dimensional Representation of Organic Molecules

The three-dimensional (3-D) structure of organic molecules can be represented on paper by using certain conventions. For example, by using solid (▬) and dashed (┈┈┈) wedge formula, the 3-D image of a molecule from a two-dimensional picture can be perceived. In these formulas the solid-wedge is used to indicate a bond projecting out of the plane of paper, towards the observer. The dashed-wedge is used to depict the bond projecting out of the plane of the paper and away from the observer. Wedges are shown in such a way that the broad end of the wedge is towards the observer. The bonds lying in plane of the paper are depicted by using a normal line (—). 3-D representation of methane molecule on paper has been shown in Fig. 12.1.

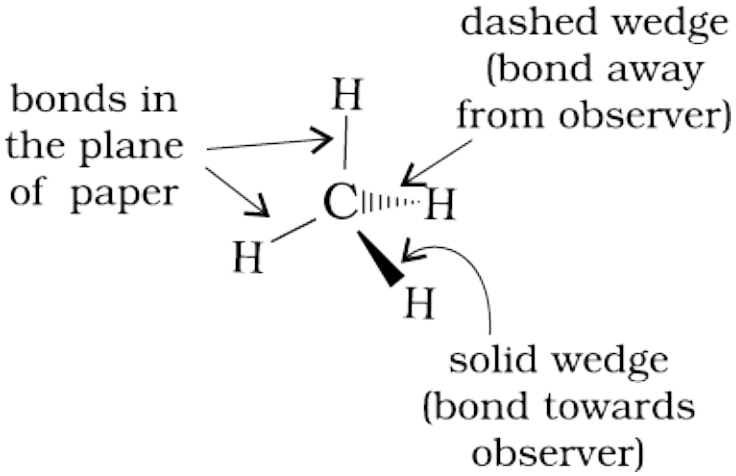


Fig. 12.1 Wedge-and-dash representation of CH4

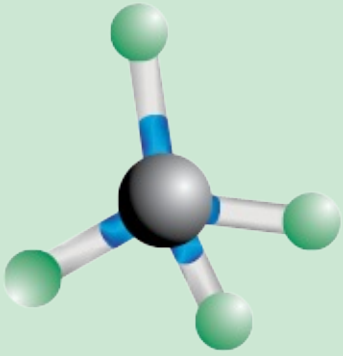
Molecular Models

Molecular models are physical devices that are used for a better visualisation and perception of three-dimensional shapes of organic molecules. These are made of wood, plastic or metal and are

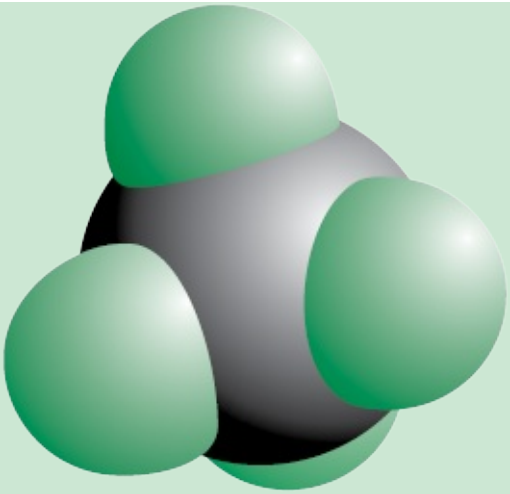
commercially available. Commonly three types of molecular models are used: (1) Framework model, (2) Ball-and-stick model, and (3) Space filling model. In the framework model only the bonds connecting the atoms of a molecule and not the atoms themselves are shown. This model emphasizes the pattern of bonds of a molecule while ignoring the size of atoms. In the ball-and-stick model, both the atoms and the bonds are shown. Balls represent atoms and the stick denotes a bond. Compounds containing C=C (e.g., ethene) can best be represented by using springs in place of sticks. These models are referred to as ball-and-spring model. The space-filling model emphasises the relative size of each atom based on its van der Waals radius. Bonds are not shown in this model. It conveys the volume occupied by each atom in the molecule. In addition to these models, computer graphics can also be used for molecular modelling.



Framework model



Ball and stick model



Space filling model

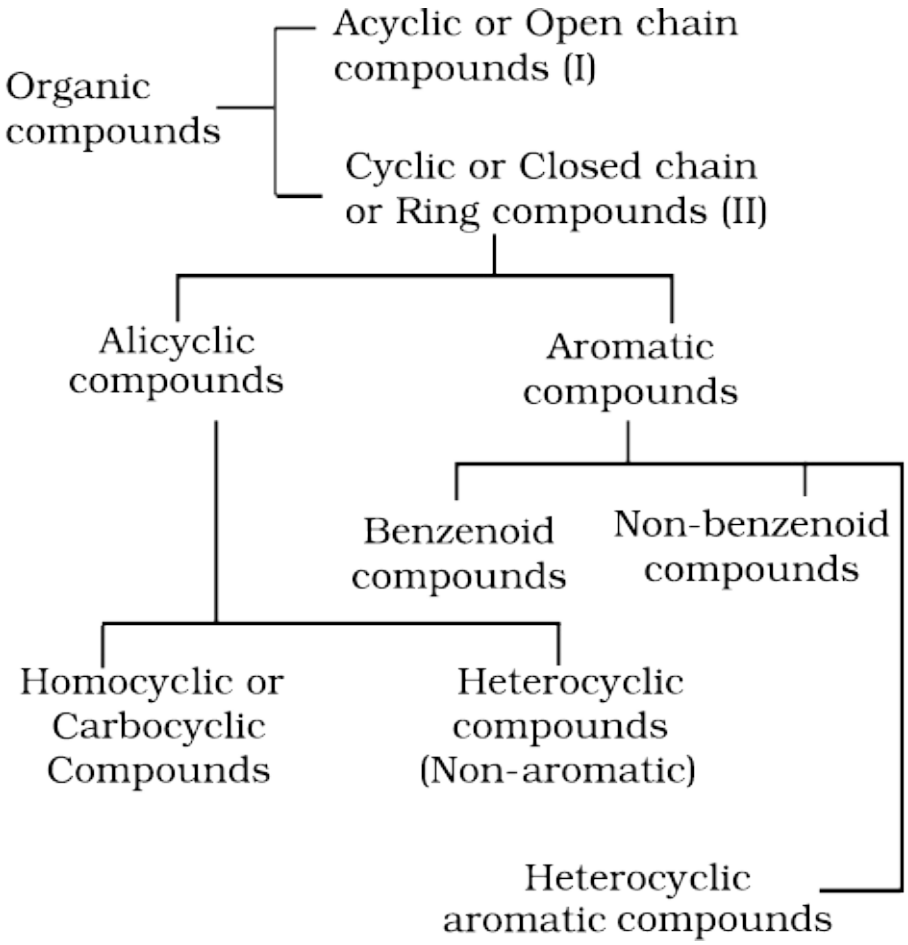
Fig. 12.2

Ethyne Methanol

Ethane Ethene

12.4 CLASSIFICATION OF ORGANIC COMPOUNDS

The existing large number of organic compounds and their ever-increasing numbers has made it necessary to classify them on the basis of their structures. Organic compounds are broadly classified as follows:

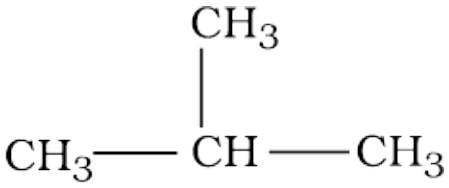


I. Acyclic or open chain compounds

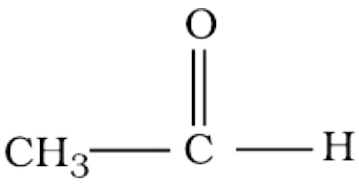
These compounds are also called as aliphatic compounds and consist of straight or branched chain compounds, for example:

CH_3CH_3

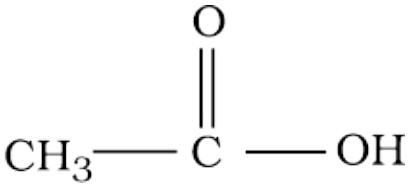
Ethane



Isobutane



Acetaldehyde

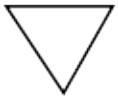


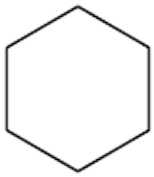
Acetic acid

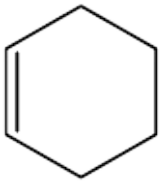
II Cyclic or closed chain or ring compounds

(a) Alicyclic compounds

Alicyclic (aliphatic cyclic) compounds contain carbon atoms joined in the form of a ring (homocyclic).



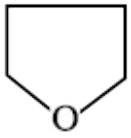




Cyclopropane Cyclohexane

Cyclohexene

Sometimes atoms other than carbon are also present in the ring (heterocylic). Tetrahydrofuran given below is an example of this type of compound:



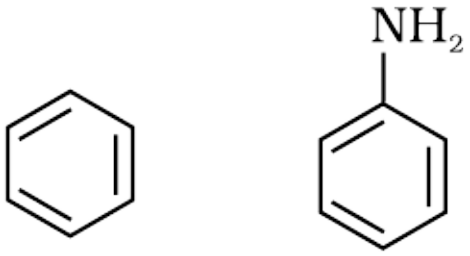
Tetrahydrofuran

These exhibit some of the properties similar to those of aliphatic compounds.

(b) Aromatic compounds

Aromatic compounds are special types of compounds. You will learn about these compounds in detail in Unit 13. These include benzene and other related ring compounds (benzenoid). Like alicyclic compounds, aromatic comounds may also have hetero atom in the ring. Such compounds are called hetrocyclic aromatic compounds. Some of the examples of various types of aromatic compounds are:

Benzenoid aromatic compounds



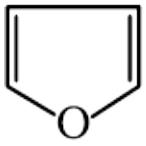
Benzene Aniline Naphthalene

Non-benzenoid compound



Tropone

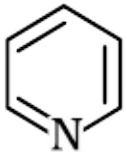
Heterocyclic aromatic compounds



Furan



Thiophene



Pyridine

Organic compounds can also be classified on the basis of functional groups, into families or homologous series.

12.4.1 Functional Group

The functional group is an atom or a group of atoms joined to the carbon chain which is responsible for the characteristic chemical properties of the organic compounds. The examples are hydroxyl group (–OH), aldehyde group (–CHO) and carboxylic acid group (–COOH) etc.

12.4.2 Homologous Series

A group or a series of organic compounds each containing a characteristic functional group forms a homologous series and the members of the series are called homologues. The members of a homologous series can be represented by general molecular formula and the successive members differ from each other in molecular formula by a –Ch2 unit. There are a number of homologous series of organic

compounds. Some of these are alkanes, alkenes, alkynes, haloalkanes, alkanols, alkanals, alkanones, alkanoic acids, amines etc.

It is also possible that a compound contains two or more identical or different functional groups. This gives rise to polyfunctional compounds.

12.5 NOMENCLATURE OF ORGANIC COMPOUNDS

Organic chemistry deals with millions of compounds. In order to clearly identify them, a systematic method of naming has been developed and is known as the IUPAC (International Union of Pure and Applied Chemistry) system of nomenclature. In this systematic nomenclature, the names are correlated with the structure such that the reader or listener can deduce the structure from the name.

Before the IUPAC system of nomenclature, however, organic compounds were assigned names based on their origin or certain properties. For instance, citric acid is named so because it is found in citrus fruits and the acid found in red ant is named formic acid since the Latin word for ant is formica. These names are traditional and are considered as trivial or common names. Some common names are followed even today. For example, Buckminsterfullerene is a common name given to the newly discovered C60 cluster (a form of carbon) noting its structural similarity to the geodesic domes popularised by the famous architect R. Buckminster Fuller. Common names are useful and in many cases indispensable, particularly when the alternative systematic names are lengthy and complicated. Common names of some organic compounds are given in Table 12.1.

Table 12.1 Common or Trivial Names of Some Organic Compounds

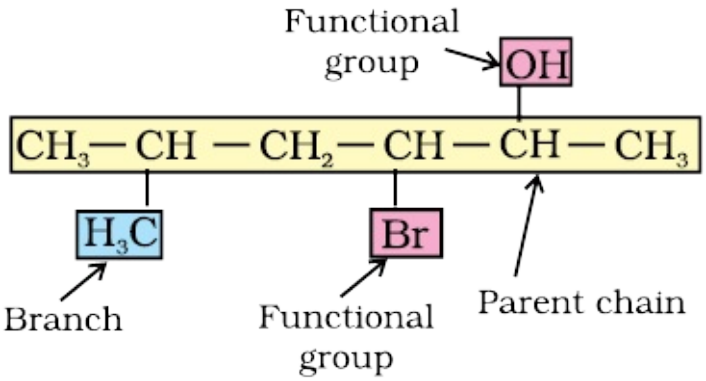
Compound	Common name
CH_4	Methane
$H_3CCH_2CH_2CH_3$	*n*-Butane
$(H_3C)_2CHCH_3$	Isobutane
$(H_3C)_4C$	Neopentane
$H_3CCH_2CH_2OH$	*n*-Propyl alcohol
HCHO	Formaldehyde
$(H_3C)_2CO$	Acetone
$CHCl_3$	Chloroform
CH_3COOH	Acetic acid
C_6H_6	Benzene
$C_6H_5OCH_3$	Anisole
$C_6H_5NH_2$	Aniline
$C_6H_5COCH_3$	Acetophenone
$CH_3OCH_2CH_3$	Ethyl methyl ether

12.5.1 The IUPAC System of Nomenclature

A systematic name of an organic compound is generally derived by identifying the parent hydrocarbon and the functional group(s) attached to it. See the example given below.

By further using prefixes and suffixes, the parent name can be modified to obtain the actual name. Compounds containing carbon and hydrogen only are called hydrocarbons. A hydrocarbon is termed saturated if it contains only carbon-carbon single bonds. The IUPAC name for a homologous series of such compounds is alkane. Paraffin (Latin: little affinity) was the earlier name given to these compounds. Unsaturated hydrocarbons are those, which contain at least one carbon-carbon

double or triple bond.



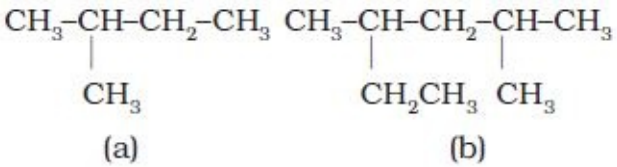
12.5.2 IUPAC Nomenclature of Alkanes

Straight chain hydrocarbons: The names of such compounds are based on their chain structure, and end with suffix '-ane' and carry a prefix indicating the number of carbon atoms present in the chain (except from CH_4 to C_4H_{10}, where the prefixes are derived from trivial names). The IUPAC names of some straight chain saturated hydrocarbons are given in Table 12.2. The alkanes in Table 12.2 differ from each other by merely the number of -CH2 groups in the chain. They are homologues of alkane series.

Table 12.2 IUPAC Names of Some Unbranched Saturated Hydrocarbons

Name	Molecular formula	Name	Molecular formula
Methane	CH_4	Heptane	C_7H_{16}
Ethane	C_2H_6	Octane	C_8H_{18}
Propane	C_3H_8	Nonane	C_9H_{20}
Butane	C_4H_{10}	Decane	$C_{10}H_{22}$
Pentane	C_5H_{12}	Icosane	$C_{20}H_{42}$
Hexane	C_6H_{14}	Triacontane	$C_{30}H_{62}$

Branched chain hydrocarbons: In a branched chain compound small chains of carbon atoms are attached at one or more carbon atoms of the parent chain. The small carbon chains (branches) are called alkyl groups. For example:



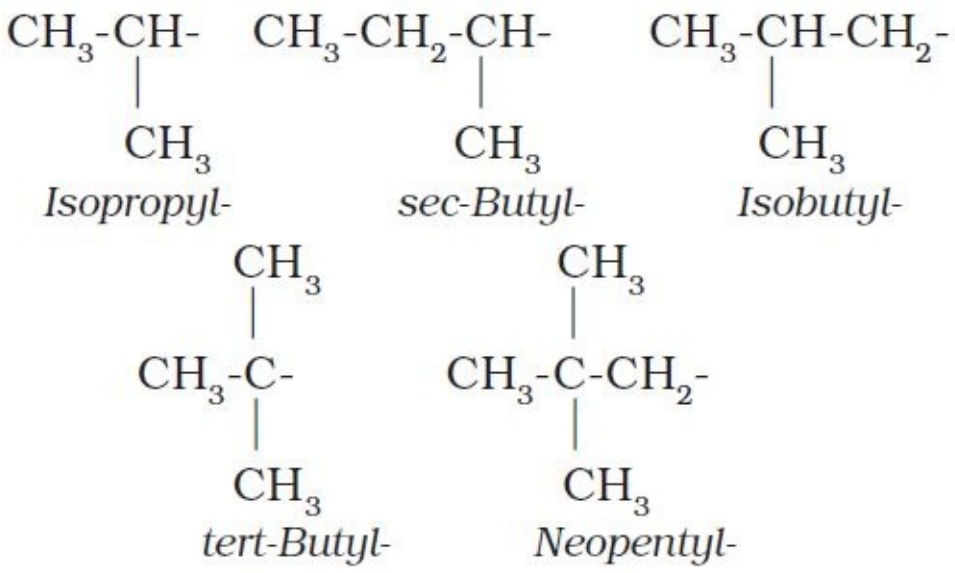
In order to name such compounds, the names of alkyl groups are prefixed to the name of parent alkane. An alkyl group is derived from a saturated hydrocarbon by removing a hydrogen atom from carbon. Thus, CH4 becomes -CH3 and is called methyl group. An alkyl group is named by substituting 'yl' for 'ane' in the corresponding alkane. Some alkyl groups are listed in Table 12.3.

Table 12.3 Some Alkyl Groups

Alkane		Alkyl group	
Molecular formula	**Name of alkane**	**Structural formula**	**Name of alkyl group**
CH_4	Methane	$-CH_3$	Methyl
C_2H_6	Ethane	$-CH_2CH_3$	Ethyl
C_3H_8	Propane	$-CH_2CH_2CH_3$	Propyl
C_4H_{10}	Butane	$-CH_2CH_2CH_2CH_3$	Butyl
$C_{10}H_{22}$	Decane	$-CH_2(CH_2)_8CH_3$	Decyl

Abbreviations are used for some alkyl groups. For example, methyl is abbreviated as Me, ethyl as Et, propyl as Pr and butyl as Bu. The alkyl groups can be branched also. Thus, propyl and butyl groups can have

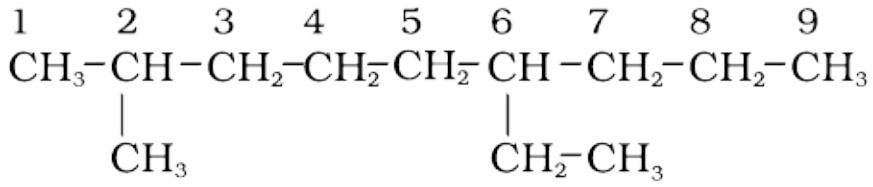
branched structures as shown below.



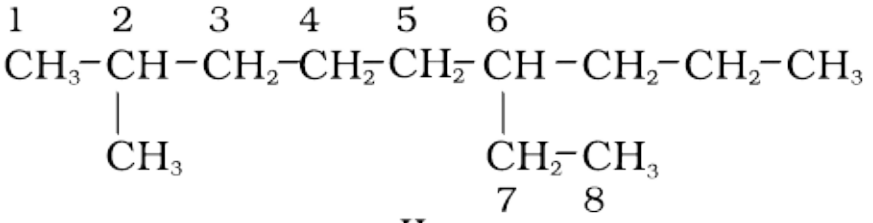
Common branched groups have specific trivial names. For example, the propyl groups can either be n-propyl group or isopropyl group. The branched butyl groups are called sec-butyl, isobutyl and tert-butyl group. We also encounter the structural unit, $–CH_2C(CH_3)_3$, which is called neopentyl group.

Nomenclature of branched chain alkanes: We encounter a number of branched chain alkanes. The rules for naming them are given below.

1. First of all, the **longest carbon chain in the molecule is identified**. In the example (I) given below, the longest chain has nine carbons and it is considered as the parent or root chain. Selection of parent chain as shown in (II) is not correct because it has only eight carbons.

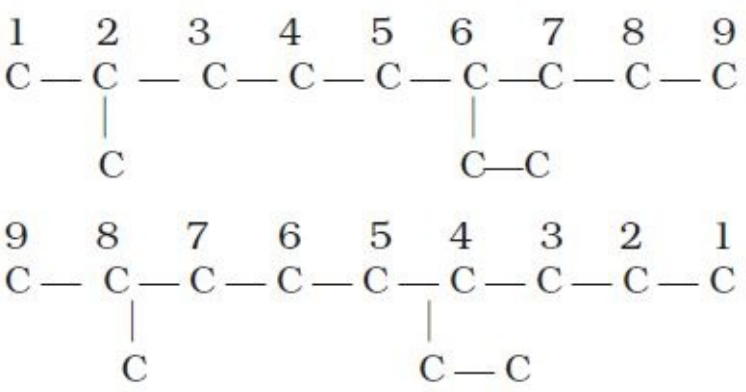


I



II

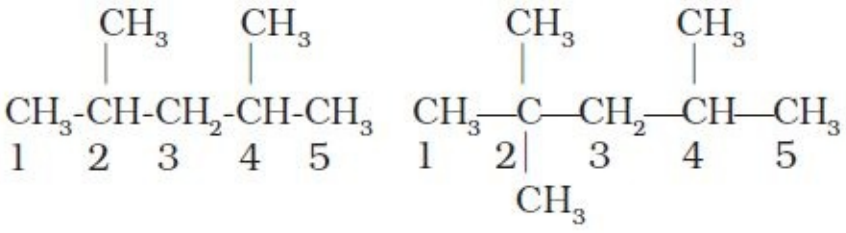
2. The carbon atoms of the parent chain are numbered to identify the parent alkane and to locate the positions of the carbon atoms at which branching takes place due to the substitution of alkyl group in place of hydrogen atoms. **The numbering is done in such a way that the branched carbon atoms get the lowest possible numbers**. Thus, the numbering in the above example should be from left to right (branching at carbon atoms 2 and 6) and not from right to left (giving numbers 4 and 8 to the carbon atoms at which branches are attached).



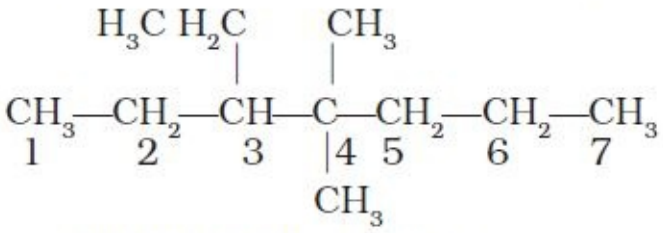
3. The names of alkyl groups attached as a branch are then prefixed to the name of the parent alkane and position of the substituents is indicated by the appropriate numbers. If different alkyl groups are present, they are listed in alphabetical order. Thus, name for the

compound shown above is: 6-ethyl-2-methylnonane. [Note: the numbers are separated from the groups by hyphens and there is no break between methyl and nonane.]

4. If two or more identical substituent groups are present then the numbers are separated by commas. The names of identical substituents are not repeated, instead prefixes such as di (for 2), tri (for 3), tetra (for 4), penta (for 5), hexa (for 6) etc. are used. While writing the name of the substituents in alphabetical order, these prefixes, however, are not considered. Thus, the following compounds are named as:

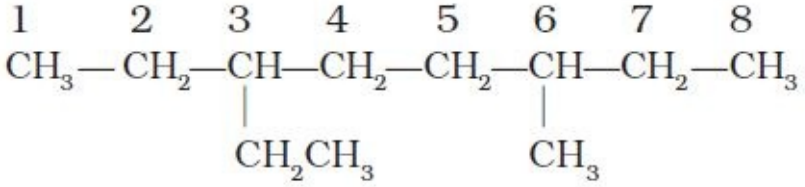


2,4-Dimethylpentane *2,2,4-Trimethylpentane*



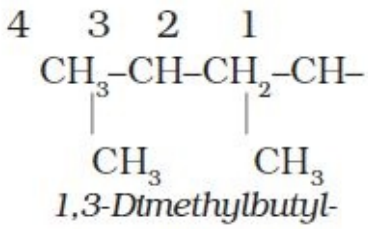
3-Ethyl-4,4-dimethylheptane

5. If the two substituents are found in equivalent positions, the lower number is given to the one coming first in the alphabetical listing. Thus, the following compound is 3-ethyl-6-methyloctane and not 6-ethyl-3-methyloctane.



6. The branched alkyl groups can be named by following the above

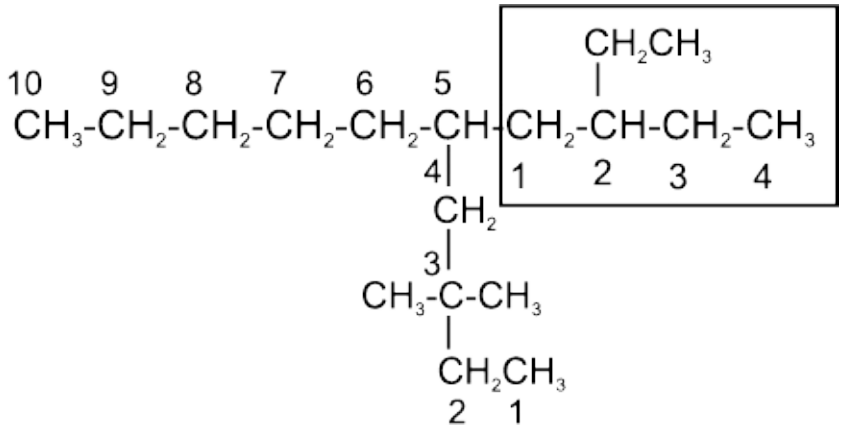
mentioned procedures. However, the carbon atom of the branch that attaches to the root alkane is numbered 1 as exemplified below.



The name of such branched chain alkyl group is placed in parenthesis while naming the compound. While writing the trivial names of substituents' **in alphabetical order, the prefixes iso- and neo- are considered to be the part of the fundamental name of alkyl group. The prefixes sec- and tert- are not** considered to be the part of the fundamental name. The use of iso and related common prefixes for naming alkyl groups is also allowed by the IUPAC nomenclature as long as these are not further substituted. In multi-substituted compounds, the following rules may aso be remembered:

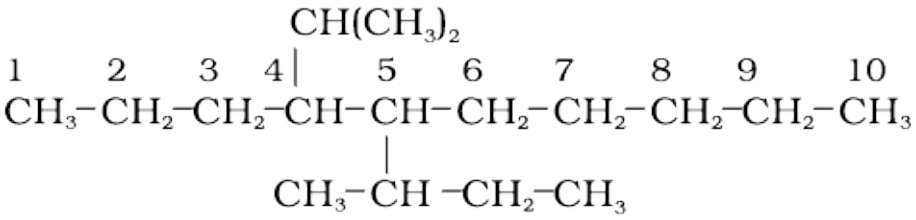
• If there happens to be two chains of equal size, then that chain is to be selected which contains more number of side chains.

• After selection of the chain, numbering is to be done from the end closer to the substituent.

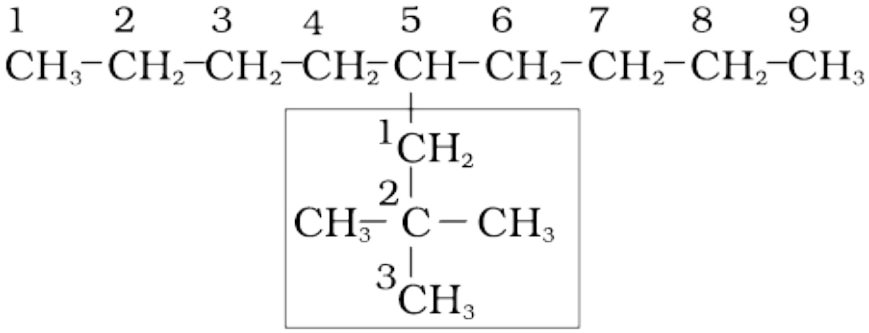


5-(2-Ethylbutyl)-3,3-dimethyldecane

[and not 5-(2,2-Dimethylbutyl)-3-ethyldecane]

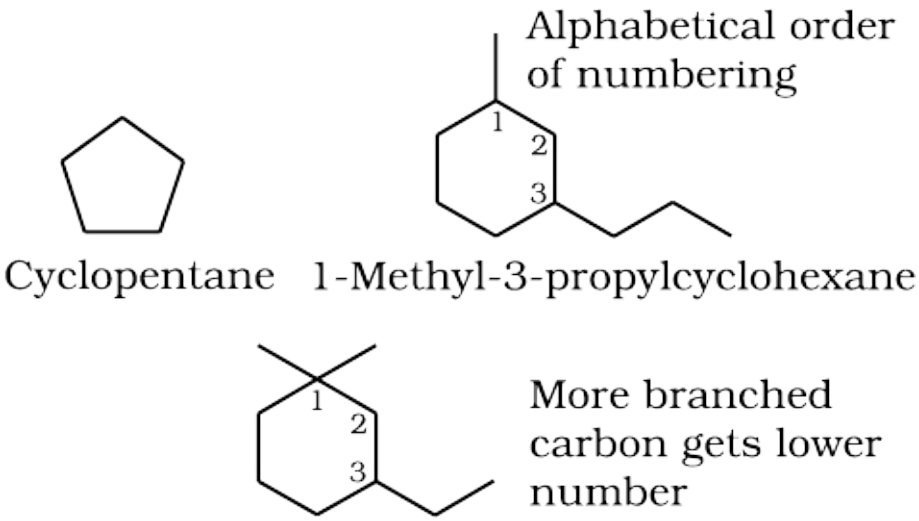


5-sec-Butyl-4-isopropyldecane



5-(2,2-Dimethylpropyl)nonane

Cyclic Compounds: A saturated monocyclic compound is named by prefixing ‘cyclo’ to the corresponding straight chain alkane. If side chains are present, then the rules given above are applied. Names of some cyclic compounds are given below.



3-Ethyl-1,1-dimethylcyclohexane

(not 1-ethyl-3,3-dimethylcyclohexane)

Problem 12.7

Structures and IUPAC names of some hydrocarbons are given below. Explain why the names given in the parentheses are incorrect.

(a) $CH_3-CH(CH_3)-CH_2-CH_2-CH(CH_3)-CH(CH_3)-CH_2-CH_3$

2,5,6- Trimethyloctane

[and not 3,4,7-Trimethyloctane]

(b) $CH_3-CH_2-CH(CH_2CH_3)-CH_2-CH(CH_3)-CH_2-CH_3$

3-Ethyl-5-methylheptane

[and not 5-Ethyl-3-methylheptane]

Solution

(a) Lowest locant number, 2,5,6 is lower than 3,5,7, (b) substituents are in equivalent position; lower number is given to the one that

comes first in the name according to alphabetical order.

12.5.3 Nomenclature of Organic Compounds having Functional Group(s)

A functional group, as defined earlier, is an atom or a group of atoms bonded together in a unique manner which is usually the site of chemical reactivity in an organic molecule. Compounds having the same functional group undergo similar reactions. For example, CH_3OH, CH_3CH_2OH, and $(CH_3)_2CHOH$ — all having -OH functional group liberate hydrogen on reaction with sodium metal. The presence of functional groups enables systematisation of organic compounds into different classes. Examples of some functional groups with their prefixes and suffixes along with some examples of organic compounds possessing these are given in Table 12.4.

First of all, the functional group present in the molecule is identified which determines the choice of appropriate suffix. **The longest chain of carbon atoms containing the functional group is numbered in such a way that the functional group is attached at the carbon atom possessing lowest possible number in the chain**. By using the suffix as given in Table 12.4, the name of the compound is arrived at.

In the case of polyfunctional compounds, one of the functional groups is chosen as the principal functional group and the compound is then named on that basis. The remaining functional groups, which are subordinate functional groups, are named as substituents using the appropriate prefixes. **The choice of principal functional group is made on the basis of order of preference. The order of decreasing priority for some functional groups is:**

-COOH, $–SO_3H$, -COOR (R=alkyl group), COCl,

$-CONH_2$, -CN,-HC=O, >C=O, -OH, $-NH_2$, >C=C<, -C≡C- .

The –R, C_6H_5-, halogens (F, Cl, Br, I), $–NO_2$, alkoxy (–OR) etc. are always prefix substituents. Thus, a compound containing both an alcohol and a keto group is named as hydroxyalkanone since the keto group is preferred to the hydroxyl group.

For example, $HOCH_2(CH_2)_3CH_2COCH_3$ will be named as 7-hydroxyheptan-2-one and not as 2-oxoheptan -7-ol. Similarly, $BrCH_2CH=CH_2$ is named as 3-bromoprop-1-ene and not 1-bromoprop-2-ene.

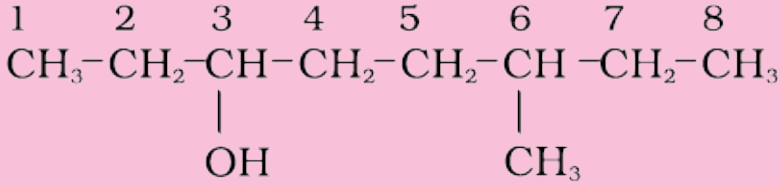
If more than one functional group of the same type are present, their number is indicated by adding di, tri, etc. before the class suffix. In such cases the full name of the parent alkane is written before the class suffix. For example $CH_2(OH)CH_2(OH)$ is named as ethane–1,2–diol. However, the ending – ne of the parent alkane is dropped in the case of compounds having more than one double or triple bond; for example, $CH_2=CH-CH=CH_2$ is named as buta–1,3–diene.

Table 12.4 Some Functional Groups and Classes of Organic Compounds

Class of compounds	Functional group structure	IUPAC group prefix	IUPAC group suffix	Example
Alkanes	-	-	-ane	Butane, $CH_3(CH_2)_2CH_3$
Alkenes	>C=C<	-	-ene	But-1-ene, $CH_2=CHCH_2CH_3$
Alkynes	-C≡C-	-	-yne	But-1-yne, $CH{\equiv}CCH_2CH_3$
Arenes	-	-	-	Benzene, 
Halides	-X (X=F,Cl,Br,I)	halo-	-	1-Bromobutane, $CH_3(CH_2)_2CH_2Br$
Alcohols	-OH	hydroxy-	-ol	Butan-2-ol, $CH_3CH_2CHOHCH_3$
Aldehydes	-CHO	formyl, or oxo	-al	Butanal, $CH_3(CH_2)_2CHO$
Ketones	>C=O	oxo-	-one	Butan-2-one, $CH_3CH_2COCH_3$
Nitriles	-C≡N	cyano	nitrile	Pentanenitrile, $CH_3CH_2CH_2CH_2CN$
Ethers	-R-O-R-	alkoxy-	-	Ethoxyethane, $CH_3CH_2OCH_2CH_3$
Carboxylic acids	-COOH	carboxy	-oic acid	Butanoic acid, $CH_3(CH_2)_2CO_2H$
Carboxylate ions	$-COO^-$	-	-oate	Sodium butanoate, $CH_3(CH_2)_2CO_2^-\ Na^+$
Esters	-COOR	alkoxycarbonyl	-oate	Methyl propanoate, $CH_3CH_2COOCH_3$
Acyl halides	-COX (X=F,Cl,Br,I)	halocarbonyl	-oyl halide	Butanoyl chloride, $CH_3(CH_2)_2COCl$
Amines	$-NH_2$, >NH,>N-	amino-	-amine	Butan -2-amine , $CH_3CHNH_2CH_2CH_3$
Amides	$-CONH_2$, -CONHR, $-CONR_2$	-carbamoyl	-amide	Butanamide, $CH_3(CH_2)_2CONH_2$
Nitro compounds	$-NO_2$	nitro	-	1-Nitrobutane, $CH_3(CH_2)_3NO_2$
Sulphonic acids	$-SO_3H$	sulpho	sulphonic acid	Methylsulphonic acid CH_3SO_3H

Problem 12.8

Write the IUPAC names of the compounds i-iv from their given structures.

(i) 

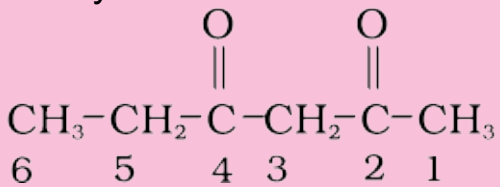
Solution

• The functional group present is an alcohol (OH). Hence the suffix is '-ol'.

• The longest chain containing -OH has eight carbon atoms. Hence the corresponding saturated hydrocarbon is octane.

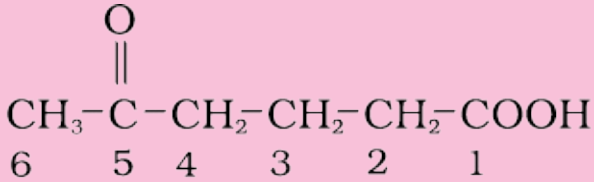
• The -OH is on carbon atom 3. In addition, a methyl group is attached at 6th carbon.

Hence, the systematic name of this compound is 6-Methyloctan-3-ol.

(ii) 

Solution

The functional group present is ketone (>C=O), hence suffix '-one'. Presence of two keto groups is indicated by 'di', hence suffix becomes 'dione'. The two keto groups are at carbons 2 and 4. The longest chain contains 6 carbon atoms, hence, parent hydrocarbon is hexane. Thus, the systematic name is Hexane-2,4-dione.

(iii) 

Solution

Here, two functional groups namely ketone and carboxylic acid are present. The principal functional group is the carboxylic acid group; hence the parent chain will be suffixed with 'oic' acid. Numbering of the chain starts from carbon of – COOH functional group. The keto group in the chain at carbon 5 is indicated by 'oxo'. The longest chain including the principal functional
group has 6 carbon atoms; hence the parent hydrocarbon is hexane. The compound is, therefore, named as
5-Oxohexanoic acid.

(iv) $\underset{6}{CH} \equiv \underset{5}{C} - \underset{4}{CH} = \underset{3}{CH} - \underset{2}{CH} = \underset{1}{CH_2}$

Solution

The two C=C functional groups are present at carbon atoms 1 and 3, while the C≡C functional group is present at carbon 5. These groups are indicated by suffixes 'diene' and 'yne' respectively. The longest chain containing the functional groups has 6 carbon atoms; hence the parent hydrocarbon is hexane. The name of compound, therefore, is Hexa-1,3-dien-5-yne.

Problem 12.9

Derive the structure of (i) 2-Chlorohexane, (ii) Pent-4-en-2-ol, (iii) 3-Nitrocyclohexene, (iv) Cyclohex-2-en-1-ol, (v) 6-Hydroxy-heptanal.

Solution

(i) 'hexane' indicates the presence of
6 carbon atoms in the chain. The functional group chloro is present at carbon 2. Hence, the structure of the compound is $CH_3CH_2CH_2CH_2CH(Cl)CH_3$.

(ii) 'pent' indicates that parent hydrocarbon contains 5 carbon atoms in the chain. 'en' and 'ol' correspond to the functional groups C=C and -OH at carbon atoms 4 and 2 respectively. Thus, the structure is

$CH_2=CHCH_2CH\ (OH)CH_3$.

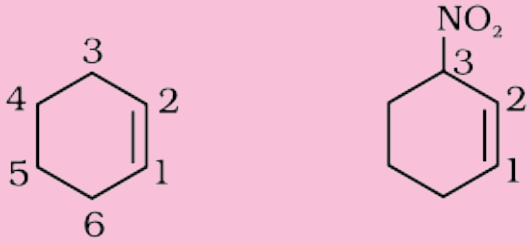
(iii) Six membered ring containing a carbon-carbon double bond is

implied by cyclohexene, which is numbered as shown in (I). The prefix 3-nitro means that a nitro group is present on C-3. Thus, complete structural formula of the compound is (II). Double bond is suffixed functional group whereas NO_2 is prefixed functional group therefore double bond gets preference over –NO2 group:



I II

(iv) '1-ol' means that a -OH group is present at C-1. OH is suffixed functional group and gets preference over C=C bond. Thus the structure is as shown
in (II):



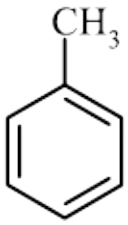
I II

(v) 'heptanal' indicates the compound to be an aldehyde containing 7 carbon atoms in the parent chain. The
'6-hydroxy' indicates that -OH group is present at carbon 6. Thus, the structural formula of the compound is: $CH_3CH(OH)CH_2CH_2CH_2CH_2CHO$. Carbon atom of –CHO group is included while numbering the carbon chain.

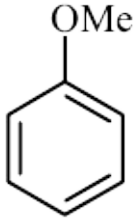
12.5.4 Nomenclature of Substituted Benzene Compounds

For IUPAC nomenclature of substituted benzene compounds, the substituent is placed as prefix to the word benzene as shown in the

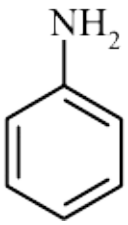
following examples. However, common names (written in bracket below) of many substituted benzene compounds are also universally used.



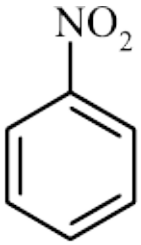
Methylbenzene
(Toluene)



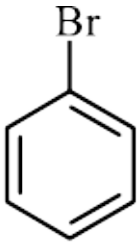
Methoxybenzene
(Anisole)



Aminobenzene
(Aniline)

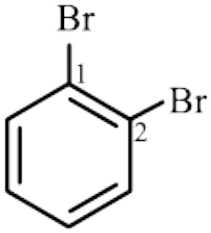


Nitrobenzene

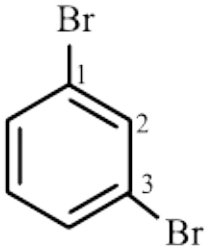


Bromobenzene

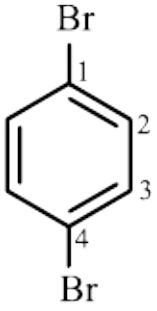
If benzene ring is disubstituted, the position of substituents is defined by numbering the carbon atoms of the ring such that the substituents are located at the lowest numbers possible.For example, the compound(b) is named as 1,3-dibromobenzene and not as 1,5-dibromobenzene.



(a) 1,2-Dibromo-benzene



(b) 1,3-Dibromo-benzene

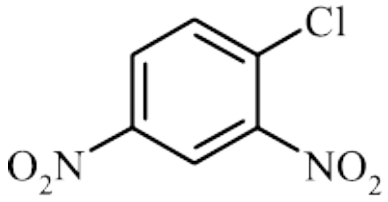


(c) 1,4-Dibromo-benzene

In the trivial system of nomenclature the terms ortho (o), meta (m) and para (p) are used as prefixes to indicate the relative positions 1,2;1,3 and 1,4 respectively. Thus,1,3-dibromobenzene (b) is named as m-dibromobenzene (meta is abbreviated as m-) and the other isomers of dibromobenzene 1,2-(a) and 1,4-(c), are named as ortho (or just o-) and para (or just p-)-dibromobenzene, respectively.

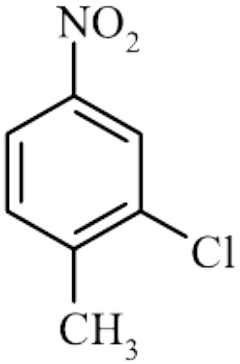
For tri - or higher substituted benzene derivatives, these prefixes cannot be used and the compounds are named by identifying substituent positions on the ring by following the lowest locant rule. In some cases, common name of benzene derivatives is taken as the base compound.

Substituent of the base compound is assigned number1 and then the direction of numbering is chosen such that the next substituent gets the lowest number. The substituents appear in the name in alphabetical order. Some examples are given below.



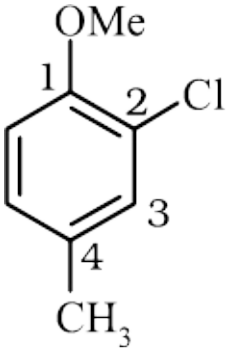
1-Chloro-2,4-dinitrobenzene

(not 4-chloro,1,3-dinitrobenzene)

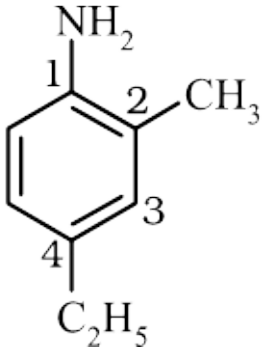


2-Chloro-1-methyl-4-nitrobenzene

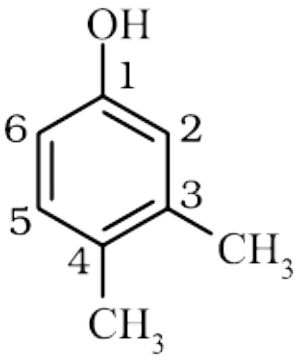
(not 4-methyl-5-chloro-nitrobenzene)



2-Chloro-4-methylanisole



4-Ethyl-2-methylaniline



3,4-Dimethylphenol

When a benzene ring is attached to an alkane with a functional group, it is considered as substituent, instead of a parent. The name for benzene as substituent is phenyl (C_6H_5-, also abbreviated as Ph).

Problem 12.10

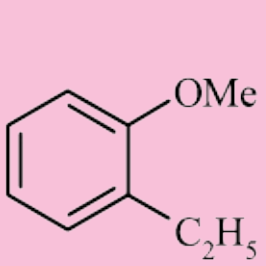
Write the structural formula of:

(a) o-Ethylanisole, (b) p-Nitroaniline,

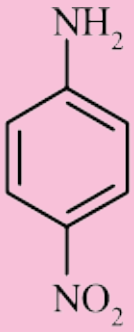
(c) 2,3 - Dibromo -1 - phenylpentane,

(d) 4-Ethyl-1-fluoro-2-nitrobenzene.

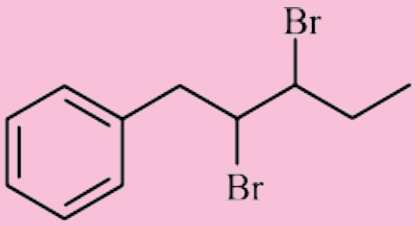
Solution



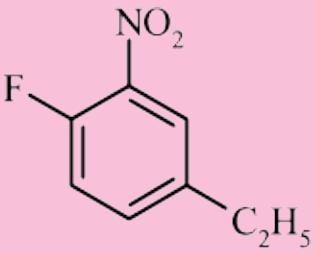
(a)



(b)



(c)



(d)

12.6 ISOMERISM

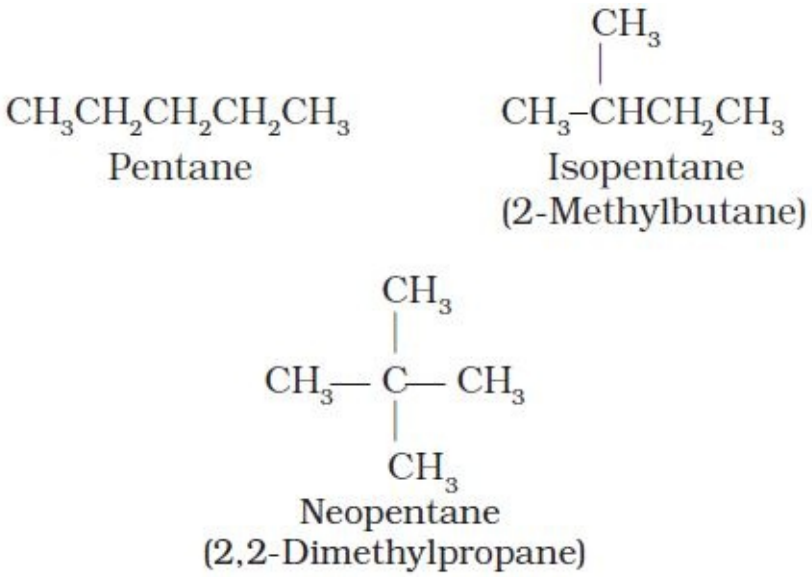
The phenomenon of existence of two or more compounds possessing the same molecular formula but different properties is known as isomerism. Such compounds are called as isomers. The following flow chart shows different types of isomerism.

12.6.1 Structural Isomerism

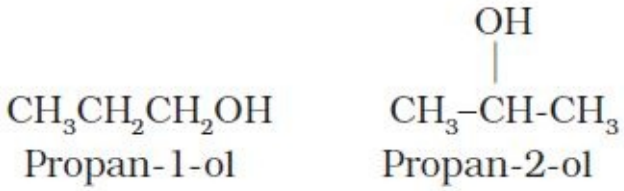
Compounds having the same molecular formula but different structures (manners in which atoms are linked) are classified as structural isomers. Some typical examples of different types of structural isomerism are

given below:

(i) Chain isomerism: When two or more compounds have similar molecular formula but different carbon skeletons, these are referred to as chain isomers and the phenomenon is termed as chain isomerism. For example, C5H12 represents three compounds:

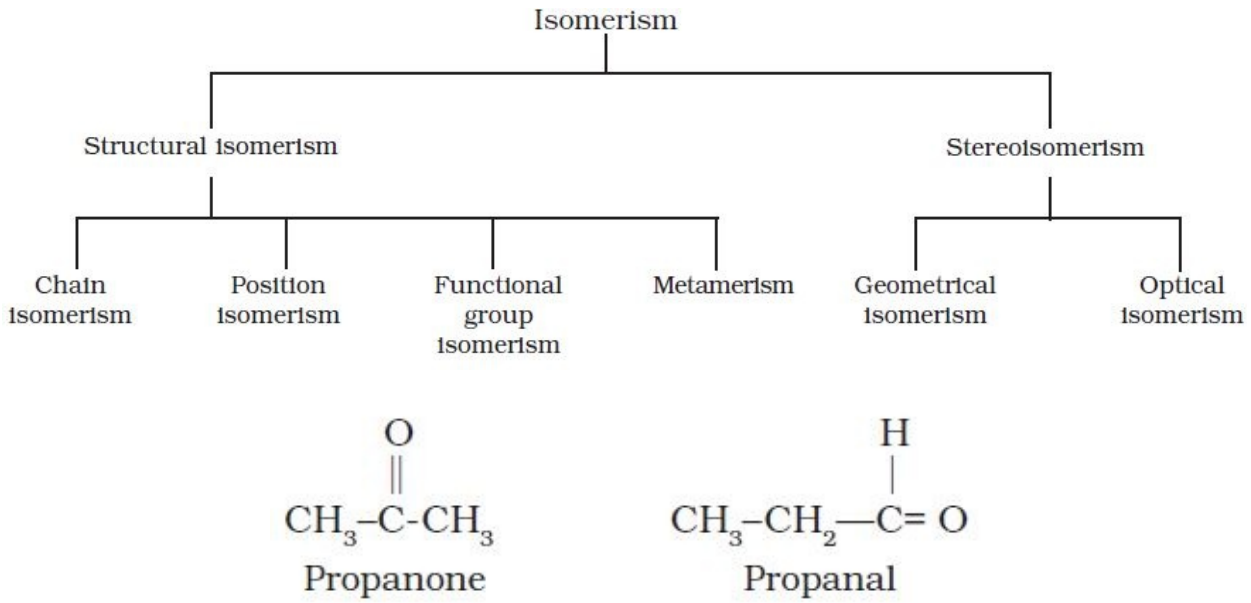


(ii) Position isomerism: When two or more compounds differ in the position of substituent atom or functional group on the carbon skeleton, they are called position isomers and this phenomenon is termed as position isomerism. For example, the molecular formula C3H8O represents two alcohols:



(iii) Functional group isomerism: Two or more compounds having the same molecular formula but different functional groups are called functional isomers and this phenomenon is termed as functional group

isomerism. For example, the molecular formula C3H6O represents an aldehyde and a ketone:



(iv) Metamerism: It arises due to different alkyl chains on either side of the functional group in the molecule. For example, $C_4H_{10}O$ represents methoxypropane ($CH_3OC_3H_7$) and ethoxyethane ($C_2H_5OC_2H_5$).

12.6.2 Stereoisomerism

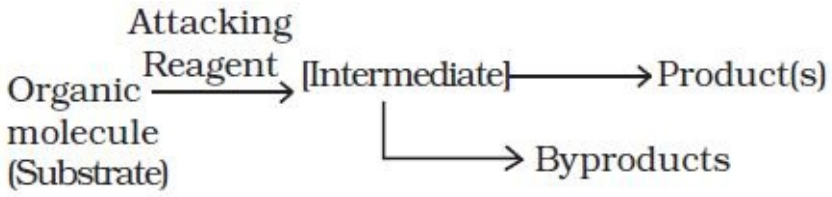
The compounds that have the same constitution and sequence of covalent bonds but differ in relative positions of their atoms or groups in space are called stereoisomers. This special type of isomerism is called as stereoisomerism and can be classified as geometrical and optical isomerism.

12.7 FUNDAMENTAL CONCEPTS IN ORGANIC REACTION MECHANISM

In an organic reaction, the organic molecule (also referred as a substrate) reacts with an appropriate attacking reagent and leads to the formation of

one or more intermediate(s) and finally product(s)

The general reaction is depicted as follows :



Substrate is that reactant which supplies carbon to the new bond and the other reactant is called reagent. If both the reactants supply carbon to the new bond then choice is arbitrary and in that case the molecule on which attention is focused is called substrate.

In such a reaction a covalent bond between two carbon atoms or a carbon and some other atom is broken and a new bond is formed. **A sequential account of each step, describing details of electron movement, energetics during bond cleavage and bond formation, and the rates of transformation of reactants into products (kinetics) is referred to as reaction mechanism.** The knowledge of reaction mechanism helps in understanding the reactivity of organic compounds and in planning strategy for their synthesis.

In the following sections, we shall learn some of the principles that explain how these reactions take place.

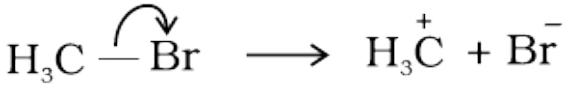
12.7.1 Fission of a Covalent Bond

A covalent bond can get cleaved either by : (i) ***heterolytic cleavage***, or by (ii) ***homolytic cleavage***.

In ***heterolytic cleavage***, the bond breaks in such a fashion that the shared pair of electrons remains with one of the fragments.

After heterolysis, one atom has a sextet electronic structure and a

positive charge and the other, a valence octet with at least one lone pair and a negative charge. Thus, heterolytic cleavage of bromomethane will give $\overset{+}{C}H_3$ and Br^- as shown below.



A species having a carbon atom possessing sextext of electrons and a positive charge is called a carbocation (earlier called carbonium ion). The $\overset{+}{C}H_3$ ion is known as a methyl cation or methyl carbonium ion. Carbocations are classified as primary, secondary or tertiary depending on whether one, two or three carbons are directly attached to the positively charged carbon. Some other examples of carbocations are: CH_3C^+H2 (ethyl cation, a primary carbocation), $(CH_3)_2C^+H$ (isopropyl cation, a secondary carbocation), and $(CH3)_3C^+$ (tert-butyl cation, a tertiary carbocation). Carbocations are highly unstable and reactive species. Alkyl groups directly attached to the positively charged carbon stabilise the carbocations due to inductive and hyperconjugation effects, which you will be studying in the sections 12.7.5 and 12.7.9. The observed order of carbocation stability is: C^+H_3 < $CH_3C^+H_2$ < $(CH3)_2C^+H$ < $(CH_3)_3C^+$. These carbocations have trigonal planar shape with positively charged carbon being sp2 hybridised. Thus, the shape of C^+H3 may be considered as being derived from the overlap of three equivalent $C(sp^2)$ hybridised orbitals with 1s orbital of each of the three hydrogen atoms. Each bond may be represented as $C(sp^2)$–H(1s) sigma bond. The remaining carbon orbital is perpendicular to the molecular plane and contains no electrons. [Fig. 12.3(a)].

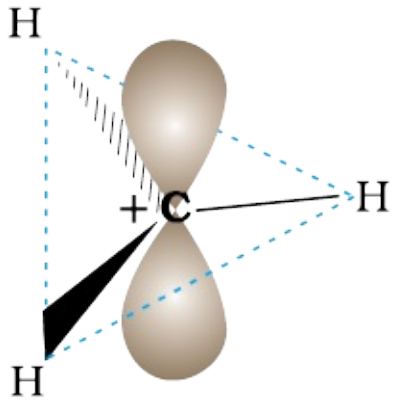


Fig. 12.3 (a) Shape of methyl carbocation

The heterolytic cleavage can also give a species in which carbon gets the shared pair of electrons. For example, when group Z attached to the carbon leaves without



electron pair, the methyl anion $\left(H_3C:^-\right)$ is

formed. Such a carbon species carrying a negative charge on carbon atom is called carbanion. Carbon in carbanion is generally sp3 hybridised and its structure is distorted tetrahedron as shown in Fig. 12.3(b).

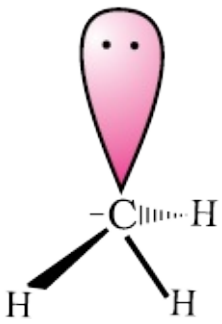
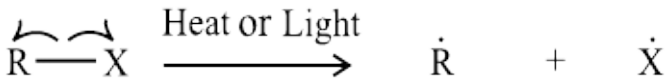


Fig. 12.3 (b) Shape of methyl carbocation

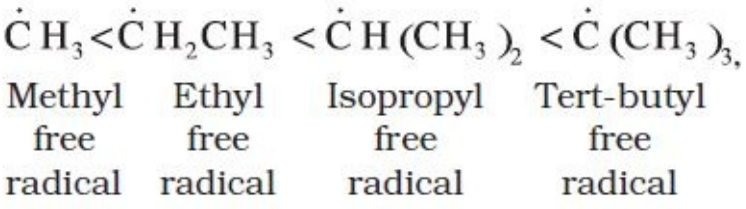
Carbanions are also unstable and reactive species. The organic reactions which proceed through heterolytic bond cleavage are called ionic or heteropolar or just polar reactions.

In homolytic cleavage, one of the electrons of the shared pair in a covalent bond goes with each of the bonded atoms. Thus, in homolytic cleavage, the movement of a single electron takes place instead of an electron pair. The single electron movement is shown by 'half-headed' (fish hook: ↷) curved arrow. Such cleavage results in the formation of neutral species (atom or group) which contains an unpaired electron. These species are called free radicals. Like carbocations and carbanions, free radicals are also very reactive. A homolytic cleavage can be shown as:



Alkyl free radical

Alkyl radicals are classified as primary, secondary, or tertiary. Alkyl radical stability increases as we proceed from primary to tertiary:



Organic reactions, which proceed by homolytic fission are called free radical or homopolar or nonpolar reactions.

12.7.2 Substrate and Reagent

Ions are generally not formed in the reactions of organic compounds. Molecules as such participate in the reaction. It is convenient to name one reagent as substrate and other as reagent. In general, a molecule whose carbon is involved in new bond formation is called substrate and the other one is called reagent. When carbon-carbon bond is formed, the

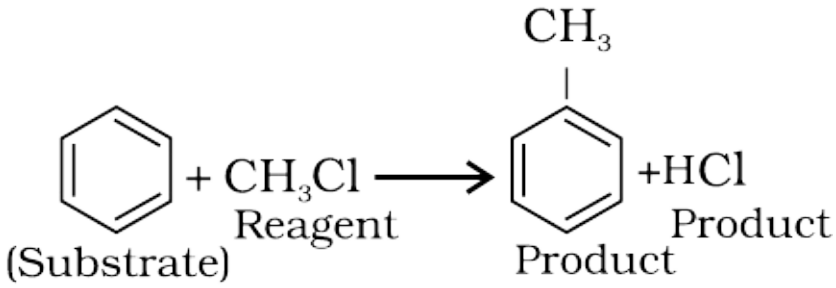
choice of naming the reactants as substrate and reagent is arbitrary and depends on molecule under observation. Example:

(i)

$$CH2 = CH2 + Br2 \longrightarrow CH2\,Br - CH2Br$$

Substrate Reagent Product

(ii)



Nucleophiles and Electrophiles

Reagents attack the reactive site of the substrate. The reactive site may be electron deficient portion of the molecule (a positive reactive site) e.g., an atom with incomplete electron shell or the positive end of the dipole in the molecule. If the attacking species is electron rich, it attacks these sites. If attacking species is electron deficient, the reactive site for it is that part of the substrate molecule which can supply electrons, e.g., π electrons in a double bond.

A reagent that brings an electron pair to the reactive site is called a **nucleophile** (Nu:) i.e., nucleus seeking and the reaction is then called **nucleophilic**. A reagent that takes away an electron pair from reactive site is called **electrophile** (E^+) i.e., electron seeking and the reaction is called **electrophilic**.

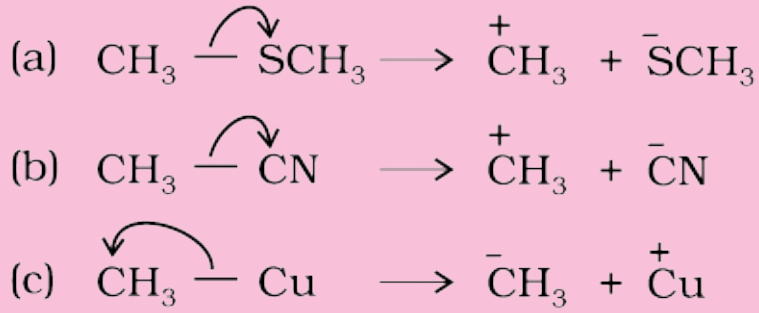
During a polar organic reaction, a nucleophile attacks an electrophilic centre of the substrate which is that specific atom or part of the substrate which is electron deficient. Similarly, the electrophiles attack at nucleophilic centre, which is the electron
rich centre of the substrate. Thus, the electrophiles receive electron pair from the substrate when the two undergo bonding interaction. A curved-arrow notation is used to show the movement of an electron pair from the nucleophile to the electrophile. Some examples of nucleophiles are the negatively charged ions with lone pair of electrons such as hydroxide (HO^-), cyanide (NC^-) ions and carbanions ($R3C:^-$). Neutral molecules such
as $H_2\ddot{O}:$, $R_3N:$, $R_2\ddot{N}H$ etc., can also act as nucleophiles due to the presence of lone pair of electrons. Examples of electrophiles include carbocations ($\overset{+}{C}H_3$) and neutral molecules having functional groups like carbonyl group (>C=O) or alkyl halides (R3C-X, where X is a halogen atom). The carbon atom in carbocations has sextet configuration; hence, it is electron deficient and can receive a pair of electrons from the nucleophiles. In neutral molecules such as alkyl halides, due to the polarity of the C-X bond a partial positive charge is generated on the carbon atom and hence the carbon atom becomes an electrophilic centre at which a nucleophile can attack.

Problem 12.11

Using curved-arrow notation, show the formation of reactive intermediates when the following covalent bonds undergo heterolytic cleavage.

(a) CH_3–SCH_3, (b) CH_3–CN, (c) CH_3–Cu

Solution



Problem 12.12

Giving justification, categorise the following molecules/ions as nucleophile or electrophile:

$HS^-, BF_3, C_2H_5O^-, (CH_3)_3N:,$

$\overset{+}{C}l, CH_3\overset{+}{C}=O, H_2N:^-, \overset{+}{N}O_2$

Solution

Nucleophiles: $HS^-, C_2H_5O^-, (CH_3)_3N:, H_2N:^-$ These species have unshared pair of electrons, which can be donated and shared with an electrophile.

Electrophiles: $BF_3, \overset{+}{C}l, CH_3-\overset{+}{C}=O, \overset{+}{N}O_2$. Reactive sites have only six valence electrons; can accept electron pair from a nucleophile.

Problem 12.13

Identify electrophilic centre in the following: $CH_3CH=O$, CH_3CN, CH_3I.

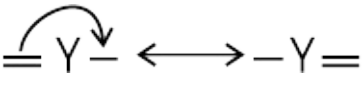
Solution

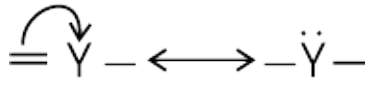
Among $CH_3HC^*=O$, $H_3CC^*\equiv N$, and
$H_3C^*–I$, the starred carbon atoms are electrophilic centers as they will have partial positive charge due to polarity of the bond.

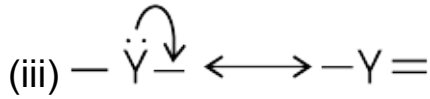
12.7.3 Electron Movement in Organic Reactions

The movement of electrons in organic reactions can be shown by curved-arrow notation. It shows how changes in bonding occur due to electronic redistribution during the reaction. To show the change in position of a pair of electrons, curved arrow starts from the point from where an electron pair is shifted and it ends at a location to which the pair of electron may move.

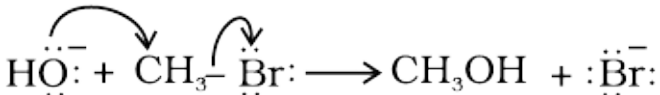
Presentation of shifting of electron pair is given below :

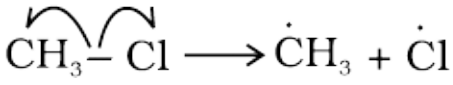
(i)  from π bond to adjacent bond position

(ii)  from π bond to adjacent atom

(iii)  from atom to adjacent bond position

Movement of single electron is indicated by a single barbed 'fish hooks' (i.e. half headed curved arrow). For example, in transfer of hydroxide ion giving ethanol and in the dissociation of chloromethane, the movement of electron using curved arrows can be depicted as follows:





12.7.4 Electron Displacement Effects in Covalent Bonds

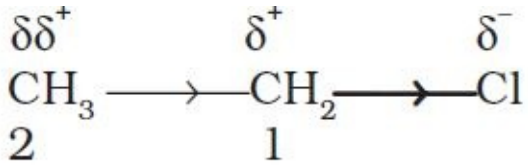
The electron displacement in an organic molecule may take place either in the ground state under the influence of an atom or a substituent group or in the presence of an appropriate attacking reagent. The electron

displacements due to the influence of an atom or a substituent group present in the molecule cause permanent polarlisation of the bond. Inductive effect and resonance effects are examples of this type of electron displacements. Temporary electron displacement effects are seen in a molecule when a reagent approaches to attack it. This type of electron displacement is called electromeric effect or polarisability effect. In the following sections we will learn about these types of electronic displacements.

12.7.5 Inductive Effect

When a covalent bond is formed between atoms of different electronegativity, the electron density is more towards the more electronegative atom of the bond. Such a shift of electron density results in a polar covalent bond. Bond polarity leads to various electronic effects in organic compounds.

Let us consider cholorethane (CH_3CH_2Cl) in which the C–Cl bond is a polar covalent bond. It is polarised in such a way that the carbon-1 gains some positive charge (δ+) and the chlorine some negative charge (δ–). The fractional electronic charges on the two atoms in a polar covalent bond are denoted by symbol δ (delta) and the shift of electron density is shown by an arrow that points from δ+ to δ– end of the polar bond.



In turn carbon-1, which has developed partial positive charge (δ+) draws some electron density towards it from the adjacent C-C bond. Consequently, some positive charge (δδ+) develops on carbon-2 also, where δδ+ symbolises relatively smaller positive charge as compared to

that on carbon – 1. In other words, the polar C – Cl bond induces polarity in the adjacent bonds. Such polarisation of σ-bond caused by the polarisation of adjacent σ-bond is referred to as the **inductive effect**. This effect is passed on to the subsequent bonds also but the effect decreases rapidly as the number of intervening bonds increases and becomes vanishingly small after three bonds. The inductive effect is related to the ability of substituent(s) to either withdraw or donate electron density to the attached carbon atom. Based on this ability, the substitutents can be classified as electron-withdrawing or electron donating groups relative to hydrogen. Halogens and many other groups such as nitro (- NO_2), cyano (- CN), carboxy (- COOH), ester (COOR), aryloxy (-OAr, e.g. – OC_6H_5), etc. are electron-withdrawing groups. On the other hand, the alkyl groups like methyl (–CH_3) and ethyl (–CH_2–CH_3) are usually considered as electron donating groups.

Problem 12.14

Which bond is more polar in the following pairs of molecules:

(a) H_3C-H, H_3C-Br

(b) H_3C-NH_2, H_3C-OH (c) H_3C-OH, H_3C-SH

Solution

(a) C–Br, since Br is more electronegative than H, (b) C–O, (c) C–O

Problem 12.15

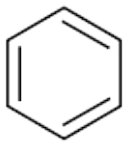
In which C–C bond of $CH_3CH_2CH_2Br$, the inductive effect is expected to be the least?

Solution

Magnitude of inductive effect diminishes as the number of intervening bonds increases. Hence, the effect is least in the bond between carbon-3 and hydrogen.

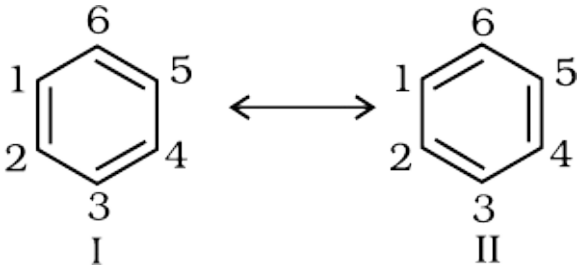
12.7.6 Resonance Structure

There are many organic molecules whose behaviour cannot be explained by a single Lewis structure. An example is that of



Benzene

benzene. Its cyclic structure containing alternating C–C single and C=C double bonds shown is inadequate for explaining its characteristic properties.

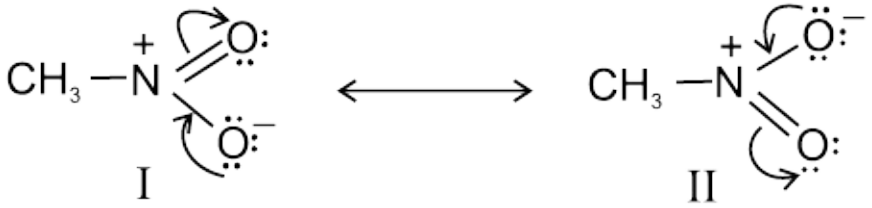


As per the above representation, benzene should exhibit two different bond lengths, due to C–C single and C=C double bonds. However, as determined experimentally benzene has a uniform C–C bond distances of 139 pm, a value intermediate between the C–C single(154 pm) and C=C double (134 pm) bonds. Thus, the structure of benzene cannot be represented adequately by the above structure. Further, benzene can be represented equally well by the energetically identical structures I and II.

Therefore, according to the resonance theory (Unit 4) the actual structure of benzene cannot be adequately represented by any of these structures, rather it is a hybrid of the two structures (I and II) called resonance structures. **The resonance structures (canonical structures or contributing structures) are hypothetical and individually do not**

represent any real molecule. They contribute to the actual structure in proportion to their stability.

Another example of resonance is provided by nitromethane (CH_3NO_2) which can be represented by two Lewis structures, (I and II). There are two types of N-O bonds in these structures.



However, it is known that the two N–O bonds of nitromethane are of the same length (intermediate between a N–O single bond and a N=O double bond). The actual structure of nitromethane is therefore a resonance hybrid of the two canonical forms I and II.

The energy of actual structure of the molecule (the resonance hybrid) is lower than that of any of the canonical structures. The difference in energy between the actual structure and the lowest energy resonance structure is called the ***resonance stabilisation energy*** or simply the ***resonance energy***. The more the number of important contributing structures, the more is the resonance energy. Resonance is particularly important when the contributing structures are equivalent in energy.

The following rules are applied while writing resonance structures:

The resonance structures have (i) the same positions of nuclei and (ii) the same number of unpaired electrons. Among the resonance structures, the one which has more number of covalent bonds, all the atoms with octet of electrons (except hydrogen which has a duplet), less separation of opposite charges, (a negative charge if any on more electronegative atom, a positive charge if any on more electropositive atom) and more dispersal of charge, is more stable than others.

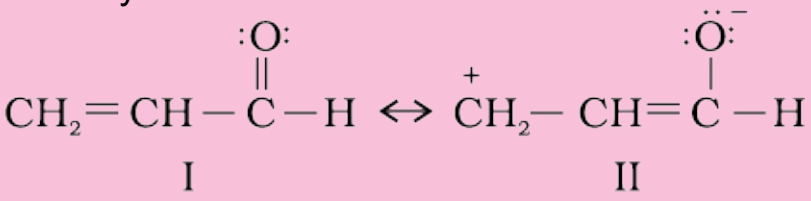
Problem 12.16

Write resonance structures of CH_3COO^- and show the movement of electrons by curved arrows.

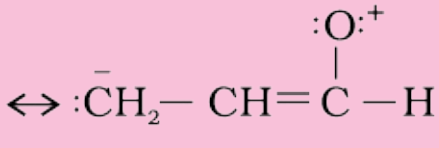
Solution

First, write the structure and put unshared pairs of valence electrons on appropriate atoms. Then draw the arrows one at a time moving the electrons to get the other structures.

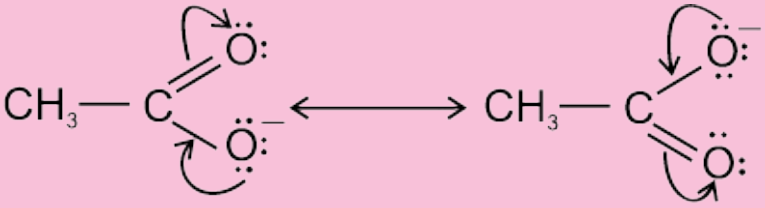
Stability: I > II > III



I II



III

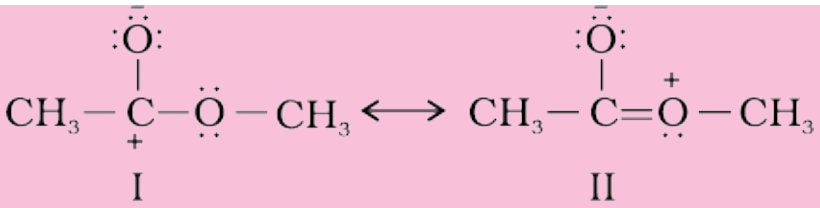


Problem 12.17

Write resonance structures of CH_2=CH–CHO. Indicate relative stability of the contributing structures.

Solution

[I: Most stable, more number of covalent bonds, each carbon and oxygen atom has an octet and no separation of opposite charge II: negative charge on more electronegative atom and positive charge on more electropositive atom; III: does not contribute as oxygen has positive charge and carbon has negative charge, hence least stable].



I II

Problem 12.18

Explain why the following two structures, I and II cannot be the major contributors to the real structure of CH_3COOCH_3.

Solution

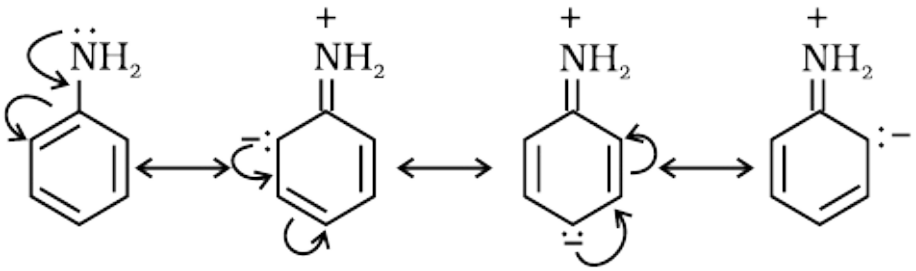
The two structures are less important contributors as they involve charge separation. Additionally, structure I contains a carbon atom with an incomplete octet.

12.7.7 Resonance Effect

The resonance effect is defined as 'the polarity produced in the molecule by the interaction of two π-bonds or between a π-bond and lone pair of electrons present on an adjacent atom'. The effect is transmitted through the chain. There are two types of resonance or mesomeric effect designated as R or M effect.

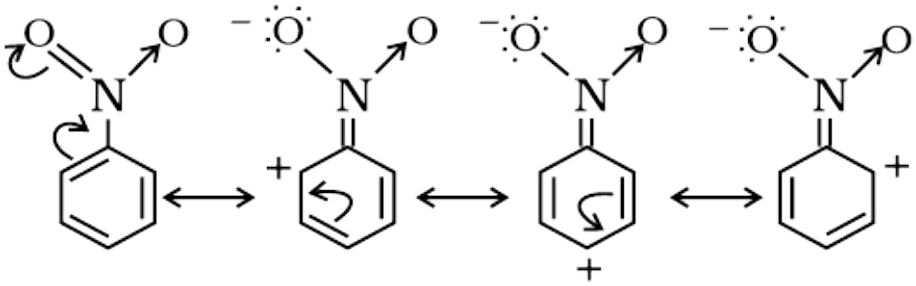
(i) Positive Resonance Effect (+R effect)

In this effect, the transfer of electrons is away from an atom or substituent group attached to the conjugated system. This electron displacement makes certain positions in the molecule of high electron densities. This effect in aniline is shown as :



(ii) Negative Resonance Effect (- R effect)

This effect is observed when the transfer of electrons is towards the atom or substituent group attached to the conjugated system. For example in nitrobenzene this electron displacement can be depicted as :



The atoms or substituent groups, which represent +R or –R electron displacement effects are as follows :

+R effect: – halogen, –OH, –OR, –OCOR, $–NH_2$, –NHR, $–NR_2$, –NHCOR,

– R effect: – COOH, –CHO, >C=O, – CN, $–NO_2$

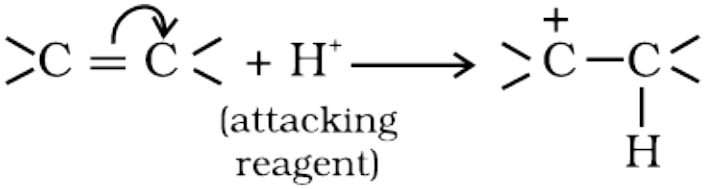
The presence of alternate single and double bonds in an open chain or cyclic system is termed as a conjugated system. These systems often show abnormal behaviour. The examples are 1,3- butadiene, aniline and nitrobenzene etc. In such systems, the π-electrons are delocalised and the system develops polarity.

12.7.8 Electromeric Effect (E effect)

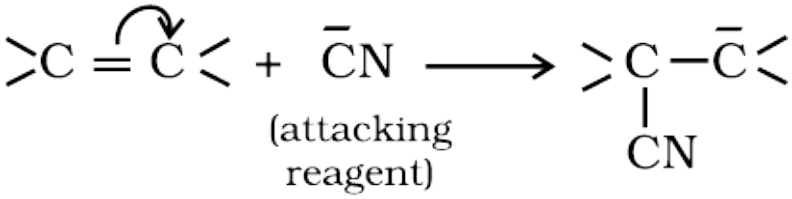
It is a temporary effect. The organic compounds having a **multiple bond** (a double or triple bond) show this effect in the presence of an attacking reagent only. It is defined as the complete transfer of a shared pair of π-electrons to one of the atoms joined by a multiple bond on the demand of an attacking reagent. The effect is annulled as soon as the attacking

reagent is removed from the domain of the reaction. It is represented by E and the shifting of the electrons is shown by a curved arrow (↷). There are two distinct types of electromeric effect.

(i) Positive Eelctromeric Effect (+E effect) In this effect the π−electrons of the multiple bond are transferred to that atom to which the reagent gets attached. For example :



(ii) Negative Electromeric Effect (–E effect) In this effect the π - electrons of the multiple bond are transferred to that atom to which the attacking reagent does not get attached. For example:



When inductive and electromeric effects operate in opposite directions, the electomeric effect predominates.

12.7.9 Hyperconjugation

Hyperconjugation is a general stabilising interaction. It involves delocalisation of σ electrons of C—H bond of an alkyl group directly attached to an atom of unsaturated system or to an atom with an unshared p orbital. The σ electrons of C—H bond of the alkyl group enter into partial conjugation with the attached unsaturated system or with the unshared p orbital. Hyperconjugation is a permanent effect.

To understand hyperconjugation effect, let us take an example of

$CH_3\overset{+}{C}H_2$ (ethyl cation) in which the positively charged carbon atom has an empty p orbital. One of the C-H bonds of the methyl group can align in the plane of this empty p orbital and the electrons constituting the C-H bond in plane with this p orbital can then be delocalised into the empty p orbital as depicted in Fig. 12.4 (a).

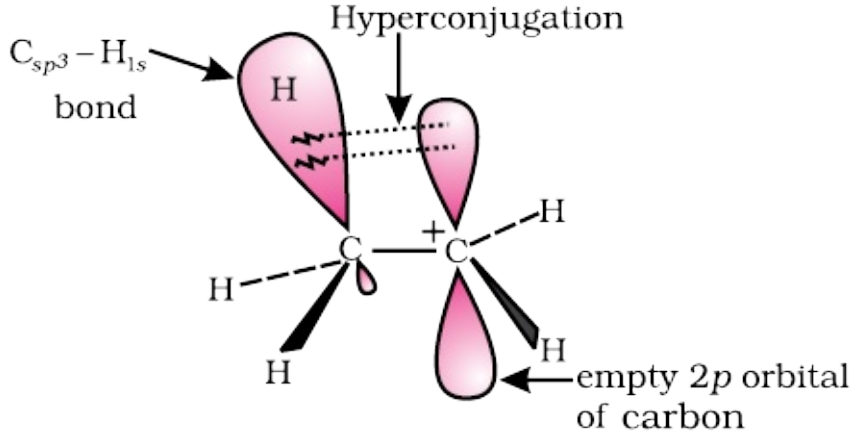
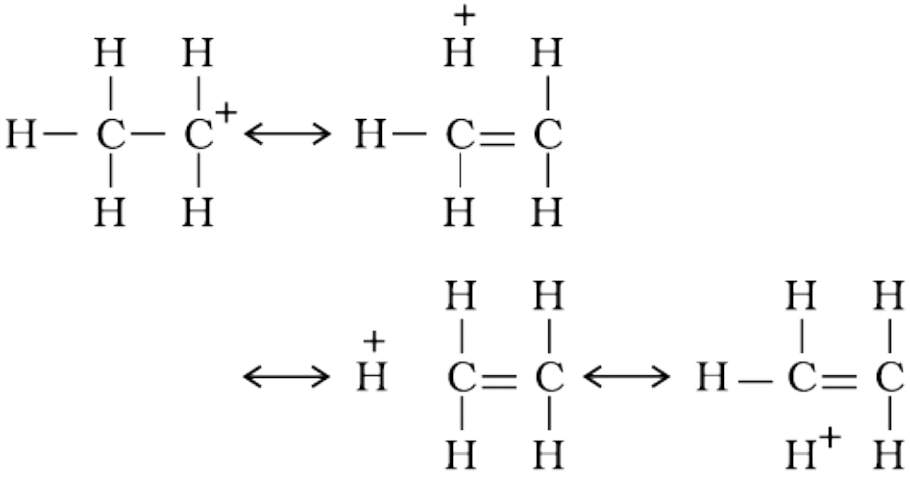


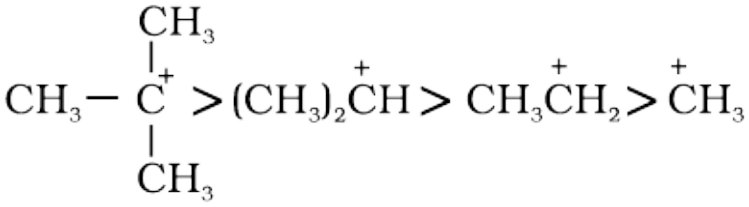
Fig. 12.4(a) Orbital diagram showing hyperconjugation in ethyl cation

This type of overlap stabilises the carbocation because electron density from the adjacent σ bond helps in dispersing the positive charge.



In general, greater the number of alkyl groups attached to a positively charged carbon atom, the greater is the hyperconjugation interaction and

stabilisation of the cation. Thus, we have the following relative stability of carbocations :



Hyperconjugation is also possible in alkenes and alkylarenes.

Delocalisation of electrons by hyperconjugation in the case of alkene can be depicted as in Fig. 12.4(b).

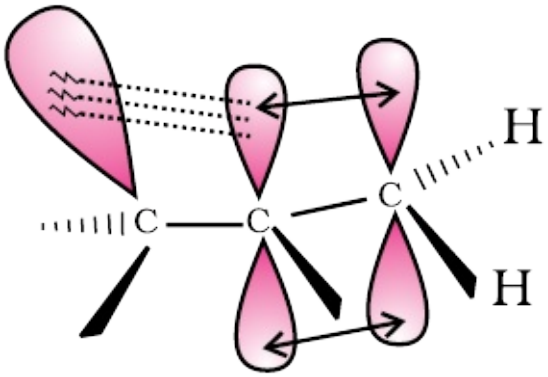
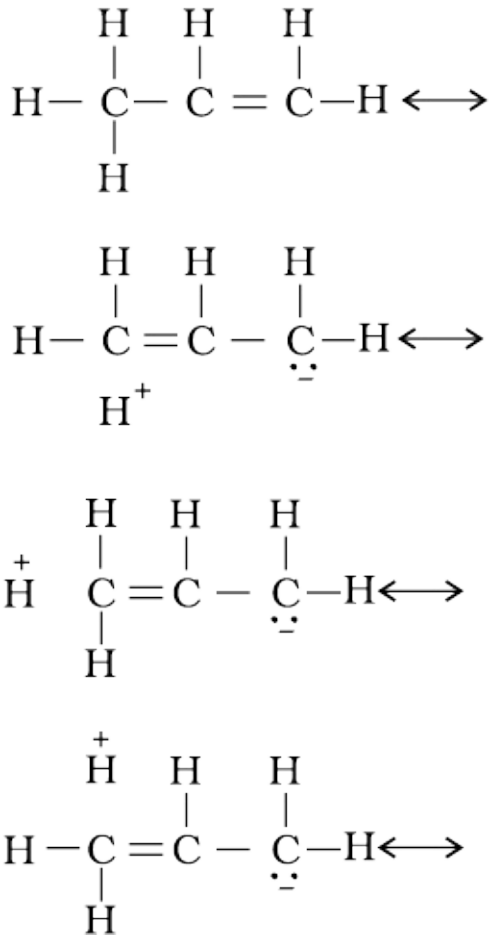


Fig. 12.4(b) Orbital diagram showing hyperconjugation in propene

There are various ways of looking at the hyperconjugative effect. One of the way is to regard C—H bond as possessing partial ionic character due to resonance.



The hyperconjugation may also be regarded as no bond resonance.

Problem 12.19

Explain why $(CH_3)_3C^+$ is more stable than $CH_3\overset{+}{C}H_2$ and $\overset{-}{C}H_3$ is the least stable cation.

Solution

Hyperconjugation interaction in $(CH_3)_3C^+$ is greater than in $CH_3\overset{+}{C}H_2$ as the $(CH_3)_3C^+$ has nine C-H bonds. In $\overset{+}{C}H_3$, vacant p orbital is perpendicular to the plane

in which C-H bonds lie; hence cannot overlap with it. Thus, $\overset{+}{C}H_3$ lacks hyperconjugative stability.

12.7.10 Types of Organic Reactions and Mechanisms

Organic reactions can be classified into the following categories:

(i) Substitution reactions

(ii) Addition reactions

(iii) Elimination reactions

(iv) Rearrangement reactions

You will be studying these reactions in Unit 13 and later in class XII.

12.8 METHODS OF PURIFICATION OF ORGANIC COMPOUNDS

Once an organic compound is extracted from a natural source or synthesised in the laboratory, it is essential to purify it. Various methods used for the purification of organic compounds are based on the nature of the compound and the impurity present in it.

The common techniques used for purification are as follows :

(i) Sublimation

(ii) Crystallisation

(iii) Distillation

(iv) Differential extraction and

(v) Chromatography

Finally, the purity of a compound is ascertained by determining its melting

or boiling point. Most of the pure compounds have sharp melting points and boiling points. New methods of checking the purity of an organic compound are based on different types of chromatographic and spectroscopic techniques.

12.8.1 Sublimation

You have learnt earlier that on heating, some solid substances change from solid to vapour state without passing through liquid state. The purification technique based on the above principle is known as sublimation and is used to separate sublimable compounds from non-sublimable impurities.

12.8.2 Crystallisation

This is one of the most commonly used techniques for the purification of solid organic compounds. It is based on the difference in the solubilities of the compound and the impurities in a suitable solvent. The impure compound is dissolved in a solvent in which it is sparingly soluble at room temperature but appreciably soluble at higher temperature. The solution is concentrated to get a nearly saturated solution. On cooling the solution, pure compound crystallises out and is removed by filtration. The filtrate (mother liquor) contains impurities and small quantity of the compound. If the compound is highly soluble in one solvent and very little soluble in another solvent, crystallisation can be satisfactorily carried out in a mixture of these solvents. Impurities, which impart colour to the solution are removed by adsorbing over activated charcoal. Repeated crystallisation becomes necessary for the purification of compounds containing impurities of comparable solubilities.

12.8.3 Distillation

This important method is used to separate (i) volatile liquids from nonvolatile impurities and (ii) the liquids having sufficient difference in their boiling points. Liquids having different boiling points vaporise at different temperatures. The vapours are cooled and the liquids so formed are collected separately. Chloroform (b.p 334 K) and aniline (b.p. 457 K) are easily separated by the technique of distillation (Fig 12.5). The liquid mixture is taken in a round bottom flask and heated carefully. On boiling, the vapours of lower boiling component are formed first. The vapours are condensed by using a condenser and the liquid is collected in a receiver. The vapours of higher boiling component form later and the liquid can be collected separately.

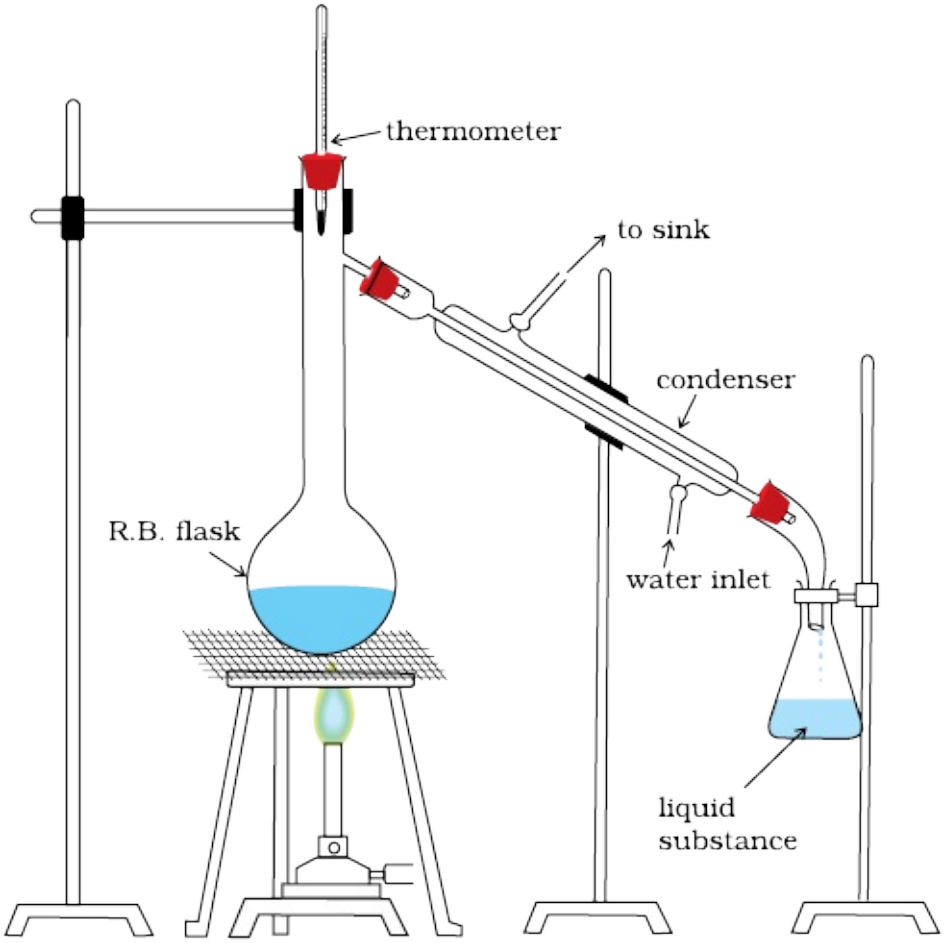


Fig.12.5 Simple distillation. The vapours of a substance formed are condensed and the liquid is collected in conical flask.

Fractional Distillation: If the difference in boiling points of two liquids is not much, simple distillation cannot be used to separate them. The vapours of such liquids are formed within the same temperature range and are condensed simultaneously. The technique of fractional distillation is used in such cases. In this technique, vapours of a liquid mixture are passed through a fractionating column before condensation. The fractionating column is fitted over the mouth of the round bottom flask (Fig.12.6, page 358).

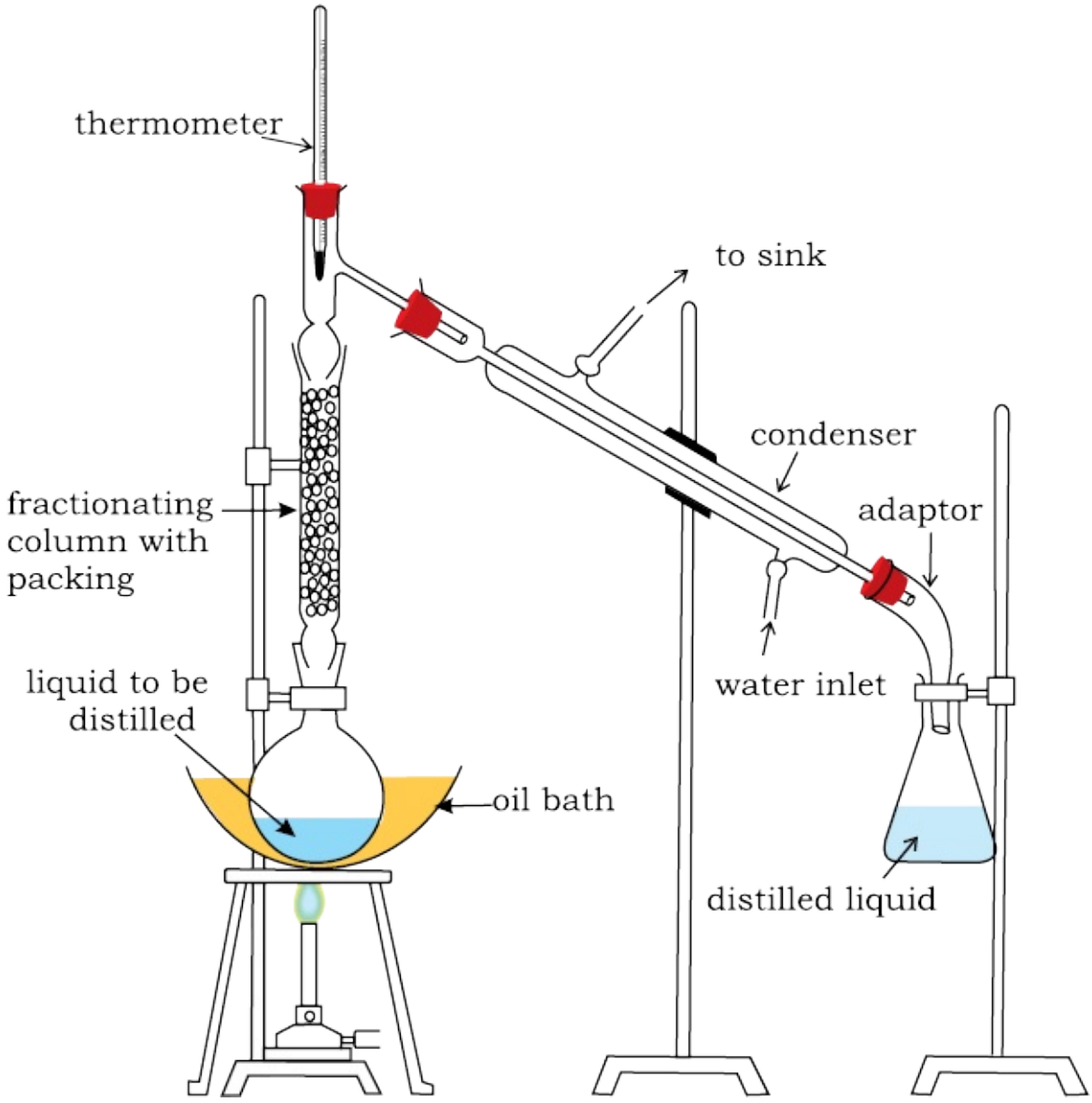


Fig.12.6 Fractional distillation. The vapours of lower boiling fraction reach the top of the column

first followed by vapours of higher boiling fractions.

Vapours of the liquid with higher boiling point condense before the vapours of the liquid with lower boiling point. The vapours rising up in the fractionating column become richer in more volatile component. By the time the vapours reach to the top of the fractionating column, these are rich in the more volatile component. Fractionating columns are available in various sizes and designs as shown in Fig.12.7. A fractionating column provides many surfaces for heat exchange between the ascending vapours and the descending condensed liquid. Some of the condensing liquid in the fractionating column obtains heat from the ascending vapours and revaporises. The vapours thus become richer in low boiling component. The vapours of low boiling component ascend to the top of the column. On reaching the top, the vapours become pure in low boiling component and pass through the condenser and the pure liquid is collected in a receiver. After a series of successive distillations, the remaining liquid in the distillation flask gets enriched in high boiling component. Each successive condensation and vaporisation unit in the fractionating column is called a theoretical plate. Commercially, columns with hundreds of plates are available.

One of the technological applications of fractional distillation is to separate different fractions of **crude oil in petroleum industry**.

Distillation under reduced pressure: This method is used to purify liquids having very high boiling points and those, which decompose at or below their boiling points. Such liquids are made to boil at a temperature lower than their normal boiling points by reducing the pressure on their surface. A liquid boils at a temperature at which its vapour pressure is equal to the external pressure. The pressure is reduced with the help of a water pump or vacuum pump (Fig.12.8). Glycerol can be separated from **spent-lye in soap industry** by using this technique.

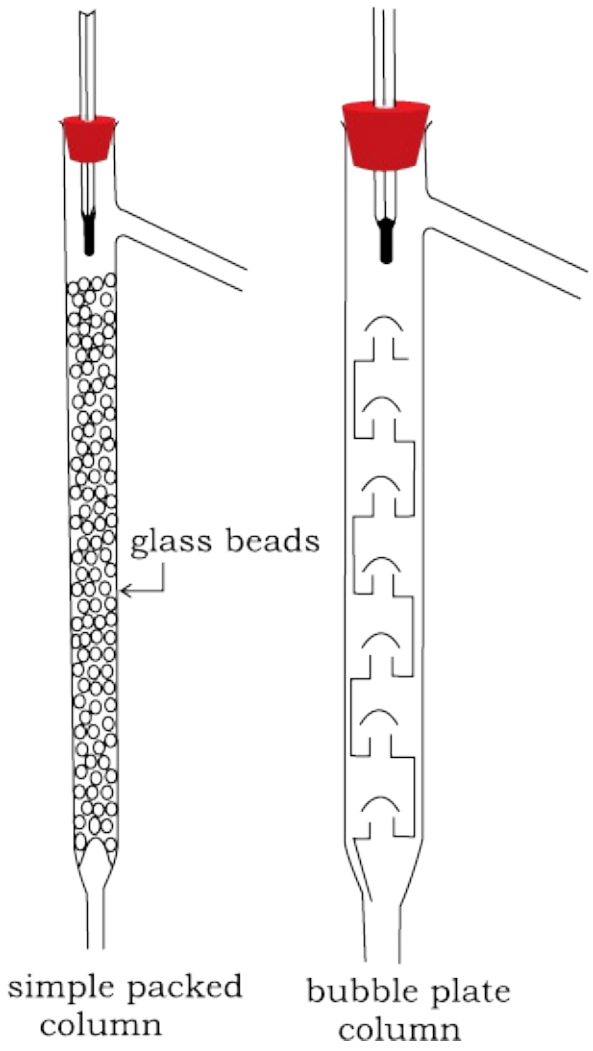
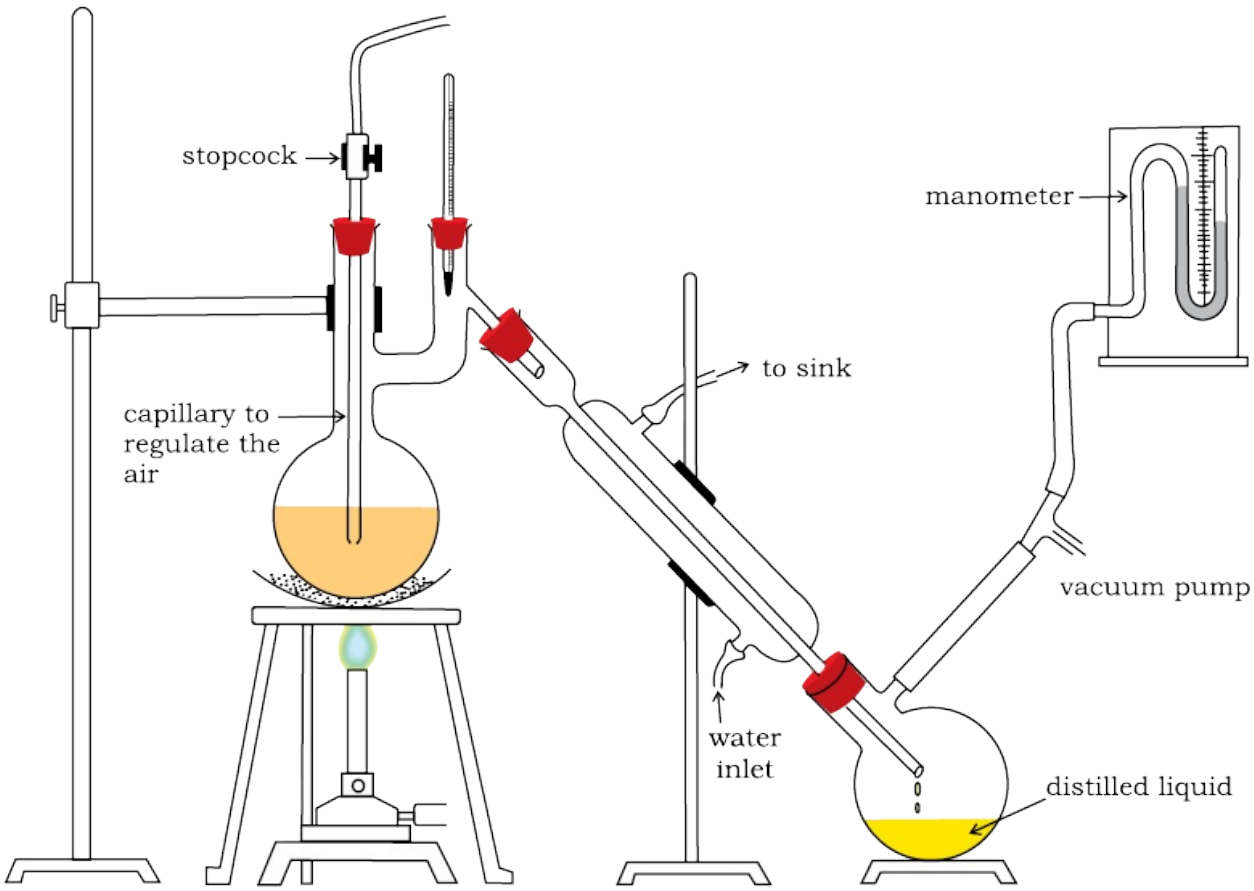


Fig.12.7 Different types of fractionating columns.

Fig.12.8 Distillation under reduced pressure. A liquid boils at a temperature below its vapour pressure by reducing the pressure.



Steam Distillation: This technique is applied to separate substances which are steam volatile and are immiscible with water. In steam distillation, steam from a steam generator is passed through a heated flask containing the liquid to be distilled. The mixture of steam and the volatile organic compound is condensed and collected. The compound is later separated from water using a separating funnel. In steam distillation, the liquid boils when the sum of vapour pressures due to the organic liquid (p_1) and that due to water (p_2) becomes equal to the atmospheric pressure (p), i.e. p =p1+ p_2. Since p1 is lower than p, the organic liquid vaporises at lower temperature than its boiling point.

Thus, if one of the substances in the mixture is water and the other, a water insoluble substance, then the mixture will boil close to but below, 373K. A mixture of water and the substance is obtained which can be

separated by using a separating funnel. Aniline is separated by this technique from aniline – water mixture (Fig.12.9, Page 360).

12.8.4 Differential Extraction

When an organic compound is present in an aqueous medium, it is separated by shaking it with an organic solvent in which it is more soluble than in water. The organic solvent and the aqueous solution should be immiscible with each other so that they form two distinct layers which can be separated by separatory funnel. The organic solvent is later removed by distillation or by evaporation to get back the compound. Differential extraction is carried out in a separatory funnel as shown in Fig. 12.10 (Page 360). If the organic compound is less soluble in the organic solvent, a very large quantity of solvent would be required to extract even a very small quantity of the compound. The technique of **continuous extraction** is employed in such cases. In this technique same solvent is repeatedly used for extraction of the compound.

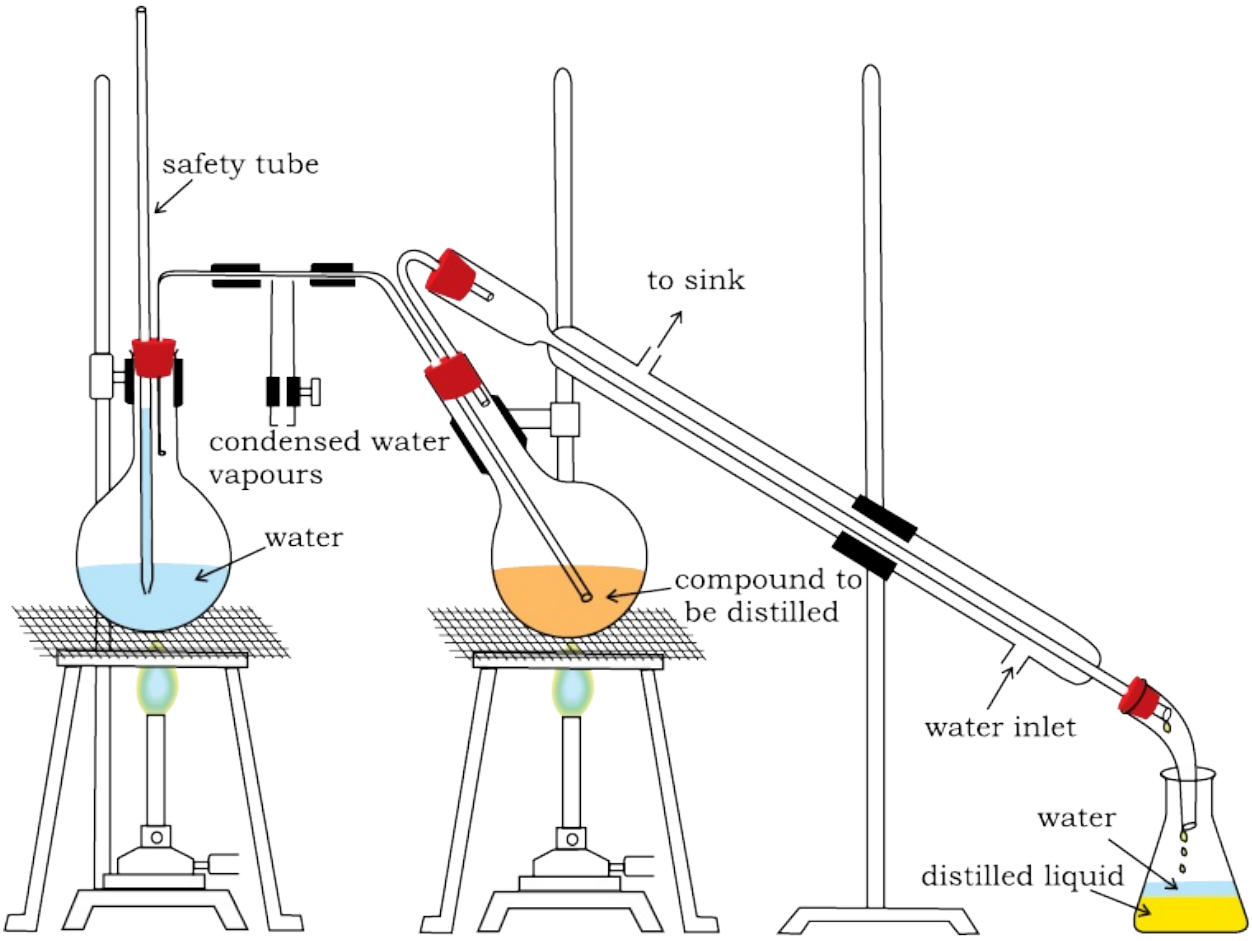


Fig.12.9 Steam distillation. Steam volatile component volatilizes, the vapours condense in the condenser and the liquid collects in conical flask.

12.8.5 Chromatography

Chromatography is an important technique extensively used to separate mixtures into their components, purify compounds and also to test the purity of compounds. The name chromatography is based on the Greek word chroma, for colour since the method was first used for the separation of coloured substances found in plants. In this technique, the mixture of substances is applied onto a stationary phase, which may be a solid or a liquid. A pure solvent, a mixture of solvents, or a gas is allowed to move slowly over the stationary phase. The components of the mixture get gradually separated from one another. The moving phase is called

the mobile phase.

Based on the principle involved, chromatography is classified into different categories. Two of these are:

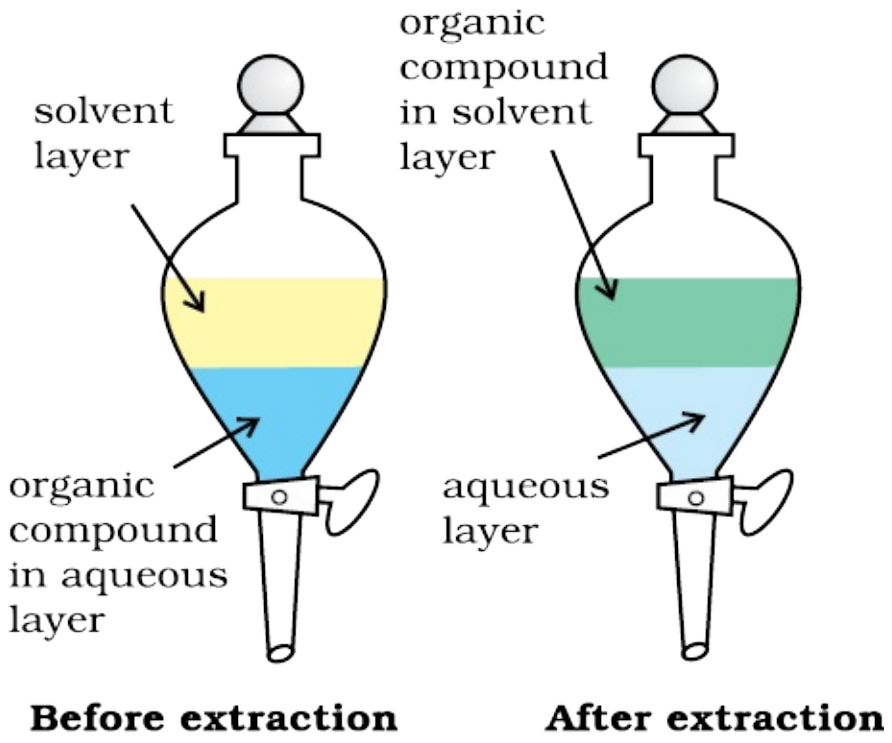


Fig.12.10 Differential extraction. Extraction of compound takes place based on difference in solubility

(a) Adsorption chromatography, and

(b) Partition chromatography.

a) Adsorption Chromatography: Adsor-ption chromatography is based on the fact that different compounds are adsorbed on an adsorbent to different degrees. Commonly used adsorbents are silica gel and alumina. When a mobile phase is allowed to move over a stationary phase (adsorbent), the components of the mixture move by varying distances over the stationary phase. Following are two main types of chromatographic techniques based on the principle of differential

adsorption.

(a) Column chromatography, and

(b) Thin layer chromatography.

Column Chromatography: Column chromatography involves separation of a mixture over a column of adsorbent (stationary phase) packed in a glass tube. The column is fitted with a stopcock at its lower end (Fig. 12.11). The mixture adsorbed on adsorbent is placed on the top of the adsorbent column packed in a glass tube. An appropriate eluant which is a liquid or a mixture of liquids is allowed to flow down the column slowly. Depending upon the degree to which the compounds are adsorbed, complete separation takes place. The most readily adsorbed substances are retained near the top and others come down to various distances in the column (Fig.12.11).

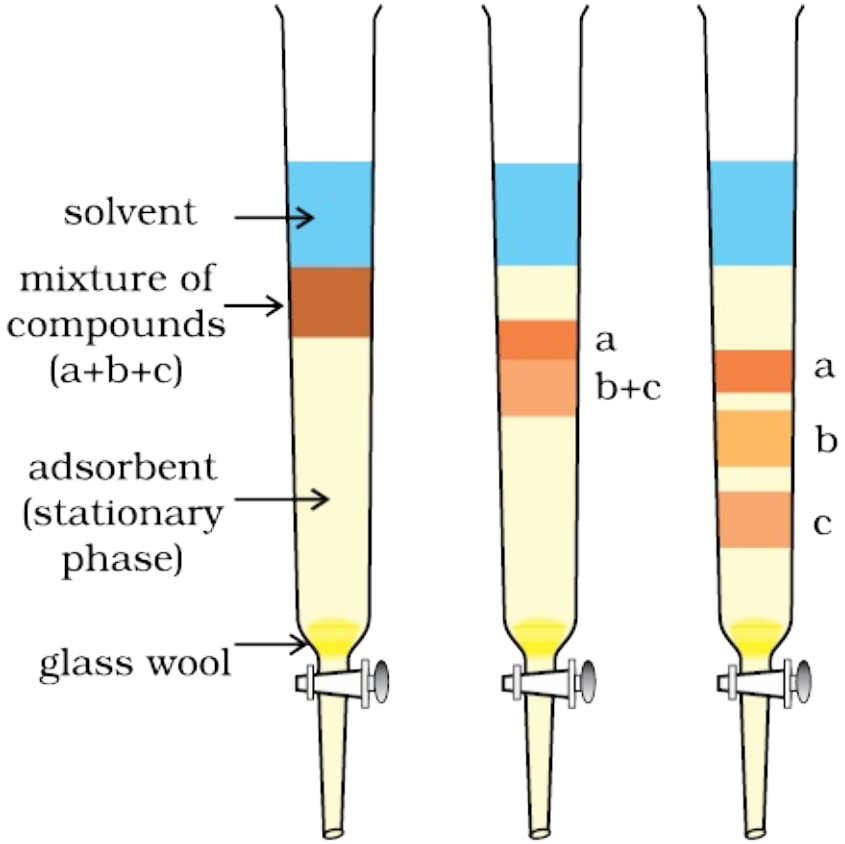


Fig.12.11 Column chromatography. Different stages of separation of components of a mixture.

Thin Layer Chromatography: Thin layer chromatography (TLC) is another type of adsorption chromatography, which involves separation of substances of a mixture over a thin layer of an adsorbent coated on glass plate. A thin layer (about 0.2mm thick) of an adsorbent (silica gel or alumina) is spread over a glass plate of suitable size. The plate is known as thin layer chromatography plate or chromaplate. The solution of the mixture to be separated is applied as a small spot about 2 cm above one end of the TLC plate. The glass plate is then placed in a closed jar containing the eluant (Fig. 12.12a). As the eluant rises up the plate, the components of the mixture move up along with the eluant to different distances depending on their degree of adsorption and separation takes place. The relative adsorption of each component of the mixture is expressed in terms of its retardation factor i.e. Rf value (Fig.12.12 b).

$$R_f = \frac{\text{Distance moved by the substance from base line (x)}}{\text{Distance moved by the solvent from base line (y)}}$$

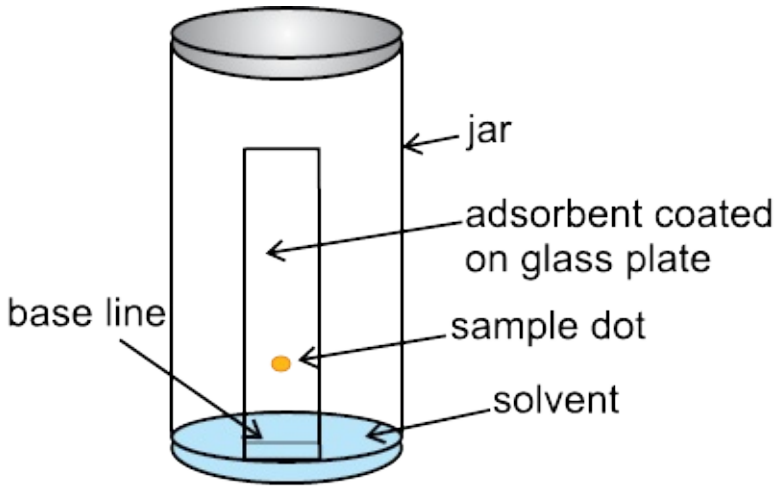


Fig.12.12 (a) Thin layer chromatography. Chromatogram being developed.

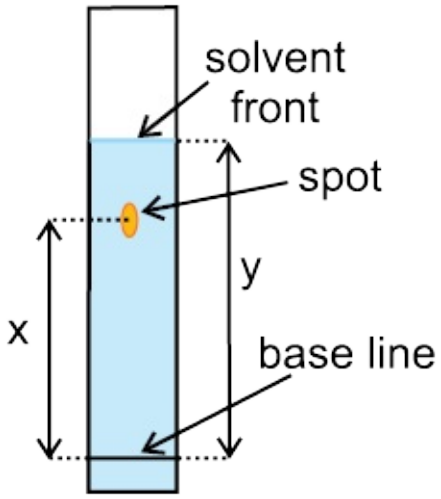


Fig.12.12 (b) Developed chromatogram.

The spots of coloured compounds are visible on TLC plate due to their original colour. The spots of colourless compounds, which are invisible to the eye but fluoresce in ultraviolet light, can be detected by putting the plate under ultraviolet light. Another detection technique is to place the plate in a covered jar containing a few crystals of iodine. Spots of compounds, which adsorb iodine, will show up as brown spots. Sometimes an appropriate reagent may also be sprayed on the plate. For example, amino acids may be detected by spraying the plate with ninhydrin solution (Fig.12.12b).

Partition Chromatography: Partition chromatography is based on continuous differential partitioning of components of a mixture between stationary and mobile phases. Paper chromatography is a type of partition chromatography. In paper chromatography, a special quality paper known as chromatography paper is used. Chromatography paper contains water trapped in it, which acts as the stationary phase.

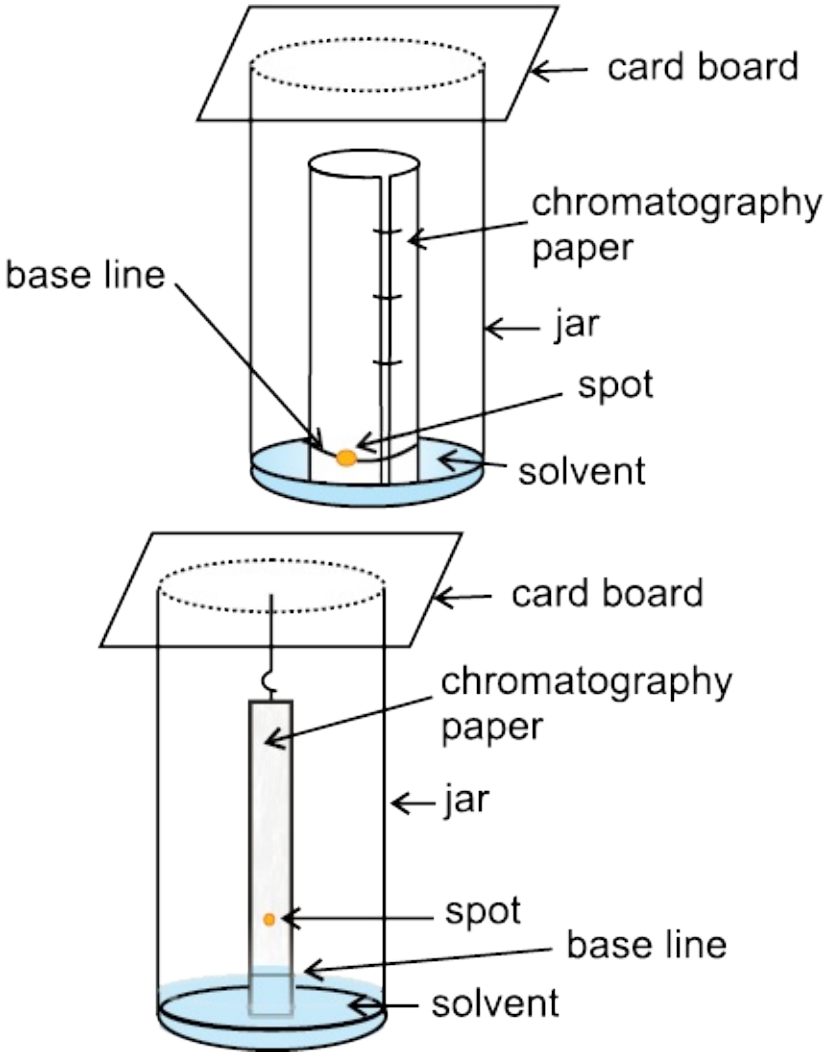


Fig.12.13 Paper chromatography. Chromatography paper in two different shapes.

A strip of chromatography paper spotted at the base with the solution of the mixture is suspended in a suitable solvent or a mixture of solvents (Fig. 12.13). This solvent acts as the mobile phase. The solvent rises up the paper by capillary action and flows over the spot. The paper selectively retains different components according to their differing partition in the two phases. The paper strip so developed is known as a chromatogram. The spots of the separated coloured compounds are visible at different heights from the position of initial spot on the chromatogram. The spots of the separated colourless compounds may be observed either under ultraviolet light or by the use of an appropriate

spray reagent as discussed under thin layer chromatography.

12.9 QUALITATIVE ANALYSIS OF ORGANIC COMPOUNDS

The elements present in organic compounds are carbon and hydrogen. In addition to these, they may also contain oxygen, nitrogen, sulphur, halogens and phosphorus.

12.9.1 Detection of Carbon and Hydrogen

Carbon and hydrogen are detected by heating the compound with copper(II) oxide. Carbon present in the compound is oxidised to carbon dioxide (tested with lime-water, which develops turbidity) and hydrogen to water (tested with anhydrous copper sulphate, which turns blue).

$$C + 2CuO \xrightarrow{\Delta} 2Cu + CO_2$$

$$2H + CuO \xrightarrow{\Delta} Cu + H_2O$$

$$CO_2 + Ca(OH)_2 \longrightarrow CaCO_3\downarrow + H_2O$$

$$5H_2O + CuSO_4 \longrightarrow CuSO_4.5H_2O$$

White Blue

12.9.2 Detection of Other Elements

Nitrogen, sulphur, halogens and phosphorus present in an organic compound are detected by “Lassaigne’s test”. The elements present in the compound are converted from covalent form into the ionic form by fusing the compound with sodium metal. Following reactions take place:

$$Na + C + N \xrightarrow{\Delta} NaCN$$

$$2Na + S \xrightarrow{\Delta} Na_2S$$

$$Na + X \xrightarrow{\Delta} Na\,X$$

(X = Cl, Br or I)

C, N, S and X come from organic compound.

Cyanide, sulphide and halide of sodium so formed on sodium fusion are extracted from the fused mass by boiling it with distilled water. This extract is known as sodium fusion extract.

(A) Test for Nitrogen

The sodium fusion extract is boiled with iron(II) sulphate and then acidified with concentrated sulphuric acid. The formation of Prussian blue colour confirms the presence of nitrogen. Sodium cyanide first reacts with iron(II)sulphate and forms sodium hexacyanidoferrate(II). On heating with concentrated sulphuric acid some iron(II) ions are oxidised to iron(III) ions which react with sodium hexacyanidoferrate(II) to produce
iron(III) hexacyanidoferrate(II) (ferriferrocyanide) which is Prussian blue in colour.

$$6CN^- + Fe^{2+} \rightarrow [Fe(CN)_6]^{4-}$$

$$3[Fe(CN)_6]^{4-} + 4Fe^{3+} \xrightarrow{xH_2O} Fe_4[Fe(CN)_6]_3.xH_2O$$

Prussian blue

(B) Test for Sulphur

(a) The sodium fusion extract is acidified with acetic acid and lead acetate is added to it. A black precipitate of lead sulphide indicates the presence of sulphur.

$S^{2-} + Pb^{2+} \longrightarrow PbS$

Black

(b) On treating sodium fusion extract with sodium nitroprusside, appearance of a violet colour further indicates the presence of sulphur.

$S^{2-} + [Fe(CN)_5NO]^{2-} \longrightarrow [Fe(CN)_5NOS]^{4-}$

Violet

In case, nitrogen and sulphur both are present in an organic compound, sodium thiocyanate is formed. It gives blood red colour and no Prussian blue since there are no free cyanide ions.

$Na + C + N + S \longrightarrow NaSCN$

$Fe^{3+} + SCN^- \longrightarrow [Fe(SCN)]^{2+}$

Blood red

If sodium fusion is carried out with excess of sodium, the thiocyanate decomposes to yield cyanide and sulphide. These ions give their usual tests.

$NaSCN + 2Na \longrightarrow NaCN + Na_2S$

(C) Test for Halogens

The sodium fusion extract is acidified with nitric acid and then treated with silver nitrate. A white precipitate, soluble in ammonium hydroxide shows the presence of chlorine, a yellowish precipitate, sparingly soluble in ammonium hydroxide shows the presence of bromine and a yellow precipitate, insoluble in ammonium hydroxide shows the presence of iodine.

$X^- + Ag^+ \longrightarrow AgX$

X represents a halogen – Cl, Br or I.

If nitrogen or sulphur is also present in the compound, the sodium fusion extract is first boiled with concentrated nitric acid to decompose cyanide or sulphide of sodium formed during Lassaigne's test. These ions would otherwise interfere with silver nitrate test for halogens.

(D) Test for Phosphorus

The compound is heated with an oxidising agent (sodium peroxide). The phosphorus present in the compound is oxidised to phosphate. The solution is boiled with nitric acid and then treated with ammonium molybdate. A yellow colouration or precipitate indicates the presence of phosphorus.

$Na_3PO_4 + 3HNO_3 \longrightarrow H_3PO_4 + 3NaNO_3$

$H_3PO_4 + 12(NH_4)_2MoO_4 + 21HNO_3 \longrightarrow$

Ammonium molybdate

$(NH_4)_3PO_4.12MoO_3 + 21NH_4NO_3 + 12H_2O$

Ammonium phosphomolybdate

12.10 QUANTITATIVE ANALYSIS

Quantitative analysis of compounds is very important in organic chemistry. It helps chemists in the determination of mass per cent of elements present in a compound. You have learnt in Unit-1 that mass per cent of elements is required for the determination of emperical and molecular formula.

The percentage composition of elements present in an organic compound is determined by the following methods:

12.10.1 Carbon and Hydrogen

Both carbon and hydrogen are estimated in one experiment. A known mass of an organic compound is burnt in the presence of excess of oxygen and copper(II) oxide. Carbon and hydrogen in the compound are oxidised to carbon dioxide and water respectively.

$$C_xH_y + (x + y/4)\, O_2 \longrightarrow x\, CO_2 + (y/2)\, H_2O$$

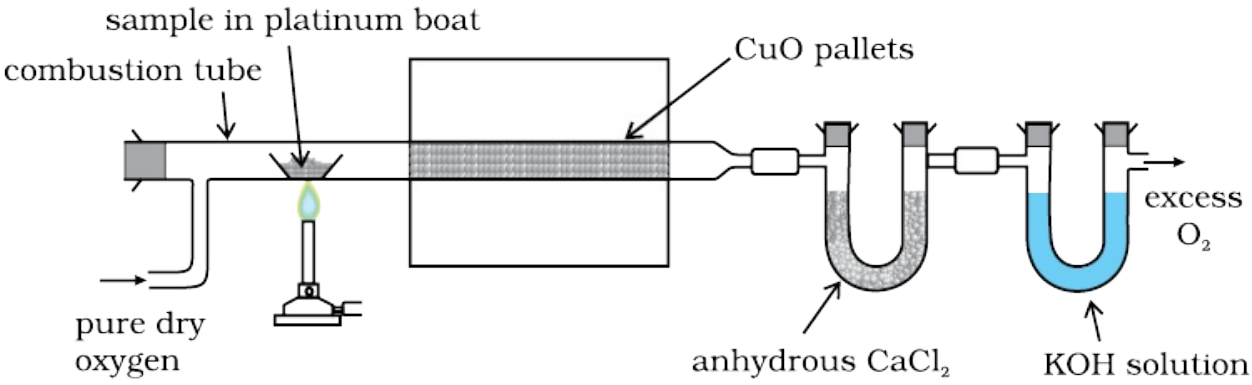


Fig.12.14 Estimation of carbon and hydrogen. Water and carbon dioxide formed on oxidation of substance are absorbed in anhydrous calcium chloride and potassium hydroxide solutions respectively contained in U tubes.

The mass of water produced is determined by passing the mixture through a weighed
U-tube containing anhydrous calcium chloride. Carbon dioxide is absorbed in another U-tube containing concentrated solution of potassium hydroxide. These tubes are connected in series (Fig.12.14). The increase in masses of calcium chloride and potassium hydroxide

gives the amounts of water and carbon dioxide from which the percentages of carbon and hydrogen are calculated.

Let the mass of organic compound be m g, mass of water and carbon dioxide produced be m1 and m2 g respectively;

Percentage of carbon= $\frac{12 \times m_2 \times 100}{44 \times m}$

Percentage of hydrogen = $\frac{2 \times m_1 \times 100}{18 \times m}$

Problem 12.20

On complete combustion, 0.246 g of an organic compound gave 0.198g of carbon dioxide and 0.1014g of water. Determine the percentage composition of carbon and hydrogen in the compound.

Solution

$$\text{Percentage of carbon} = \frac{12 \times 0.198 \times 100}{44 \times 0.246}$$
$$= 21.95\%$$

Percentage of hydrogen = $\frac{2 \times 0.1014 \times 100}{18 \times 0.246}$

= 4.58%

12.10.2 Nitrogen

There are two methods for estimation of nitrogen: (i) Dumas method and (ii) Kjeldahl's method.

(i) Dumas method: The nitrogen containing organic compound, when heated with copper oxide in an atmosphere of carbon dioxide, yields free nitrogen in addition to carbon dioxide and water.

$$C_xH_yN_z + (2x + y/2)\ CuO \longrightarrow x\ CO_2 + y/2\ H_2O + z/2\ N_2 + (2x + y/2)\ Cu$$

Traces of nitrogen oxides formed, if any, are reduced to nitrogen by passing the gaseous mixture over a heated copper gauze. The mixture of gases so produced is collected over an aqueous solution of potassium hydroxide which absorbs carbon dioxide. Nitrogen is collected in the upper part of the graduated tube (Fig.12.15).

Let the mass of organic compound = m g

Volume of nitrogen collected = V1 mL

Room temperature = T1K

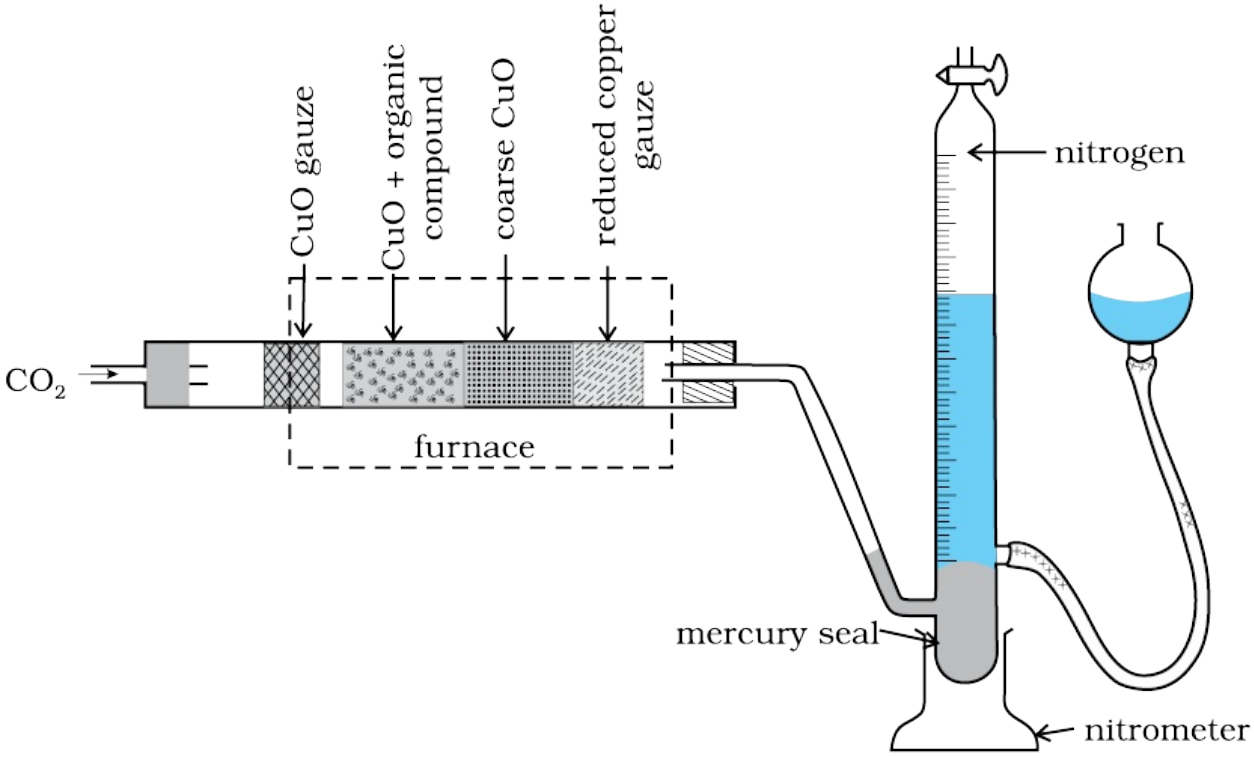


Fig.12.15 Dumas method. The organic compound yields nitrogen gas on heating it with copper(II) oxide in the presence of CO2 gas. The mixture of gases is collected over potassium hydroxide

solution in which CO2 is absorbed and volume of nitrogen gas is determined.

$$\text{Volume of nitrogen at STP} = \frac{p_1 V_1 \times 273}{760 \times T_1}$$

(Let it be V mL)

Where p1 and V1 are the pressure and volume of nitrogen, p1 is different from the atmospheric pressure at which nitrogen gas is collected. The value of p1 is obtained by the relation;

p1= Atmospheric pressure – Aqueous tension

22400 mL N2 at STP weighs 28 g.

$$V \text{ mL } N_2 \text{ at STP weighs} = \frac{28 \times V}{22400} \text{g}$$

$$\text{Percentage of nitrogen} = \frac{28 \times V \times 100}{22400 \times m}$$

Problem 12.21

In Dumas' method for estimation of nitrogen, 0.3g of an organic compound gave 50mL of nitrogen collected at 300K temperature and 715mm pressure. Calculate the percentage composition of nitrogen in the compound. (Aqueous tension at 300K=15 mm)

Solution

Volume of nitrogen collected at 300K and 715mm pressure is 50 mL

Actual pressure = 715-15 =700 mm

$$\text{Volume of nitrogen at STP} = \frac{273 \times 700 \times 50}{300 \times 760}$$

$$= 41.9 \text{ mL}$$

22,400 mL of N2 at STP weighs = 28 g

$$41.9 \text{ mL of nitrogen weighs} = \frac{28 \times 41.9}{22400} \text{ g}$$

$$\text{Percentage of nitrogen} = \frac{28 \times 41.9 \times 100}{22400 \times 0.3}$$

$$= 17.46\%$$

(ii) Kjeldahl's method: The compound containing nitrogen is heated with concentrated sulphuric acid. Nitrogen in the compound gets converted to ammonium sulphate (Fig. 12.16). The resulting acid mixture is then heated with excess of sodium hydroxide. The liberated ammonia gas is absorbed in an excess of standard solution of sulphuric acid. The amount of ammonia produced is determined by estimating the amount of sulphuric acid consumed in the reaction. It is done by estimating unreacted sulphuric acid left after the absorption of ammonia by titrating it with standard alkali solution. The difference between the initial amount of acid taken and that left after the reaction gives the amount of acid reacted with ammonia.

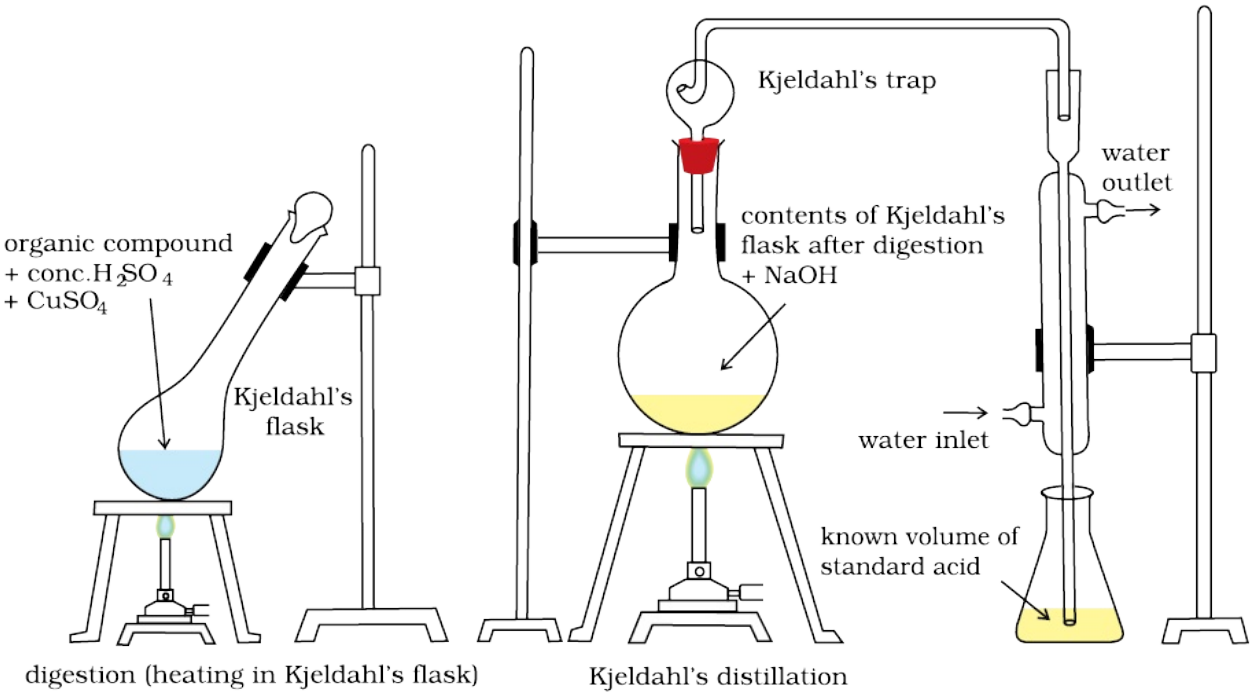


Fig.12.16 Kjeldahl method. Nitrogen-containing compound is treated with concentrated H2SO4 to get ammonium sulphate which liberates ammonia on treating with NaOH; ammonia is absorbed in known volume of standard acid.

Organic compound + $H_2SO_4 \longrightarrow (NH_4)_2SO_4$

$$\xrightarrow{2NaOH} Na_2SO_4 + 2NH_3 + 2H_2O$$

$2NH_3 + H_2SO_4 \longrightarrow (NH_4)_2SO_4$

Let the mass of organic compound taken = m g

Volume of H_2SO_4 of molarity, M,

taken = V mL

Volume of NaOH of molarity, M, used for titration of excess of H_2SO_4 = V1 mL

V1mL of NaOH of molarity M

= V1 /2 mL of H_2SO_4 of molarity M

Volume of H_2SO_4 of molarity M unused

= (V - V1/2) mL

(V- V1/2) mL of H_2SO_4 of molarity M

= 2(V-V1/2) mL of NH_3 solution of molarity M.

1000 mL of 1 M NH_3 solution contains

17g NH_3 or 14 g of N

2(V-V1/2) mL of NH3 solution of molarity M contains:

$$\frac{14 \times M \times 2(V - V_1/2)}{1000} \text{ g N}$$

$$\text{Percentage of N} = \frac{14 \times M \times 2(V - V_1/2)}{1000} \times \frac{100}{m}$$

$$= \frac{1.4 \times M \times 2(V - V_1/2)}{m}$$

Kjeldahl method is not applicable to compounds containing nitrogen in nitro and azo groups and nitrogen present in the ring (e.g. pyridine) as nitrogen of these compounds does not change to ammonium sulphate under these conditions.

Problem 12.22

During estimation of nitrogen present in an organic compound by Kjeldahl's method, the ammonia evolved from 0.5 g of the compound in Kjeldahl's estimation of nitrogen, neutralized 10 mL of 1 M H2SO4. Find out the percentage of nitrogen in the compound.

Solution

1 M of 10 mL H_2SO_4=1M of 20 mL NH_3

1000 mL of 1M ammonia contains 14 g nitrogen

Fig. 12.17 Carius method. Halogen containing organic compound is heated with fuming nitric acid in the presence of silver nitrate.

20 mL of 1M ammonia contains $\frac{14 \times 20}{1000}$ g nitrogen

$$\text{Percentage of nitrogen} = \frac{14 \times 20 \times 100}{1000 \times 0.5} = 56.0\%$$

12.10.3 Halogens

Carius method: A known mass of an organic compound is heated with fuming nitric acid in the presence of silver nitrate contained in a hard glass tube known as Carius tube, (Fig.12.17)

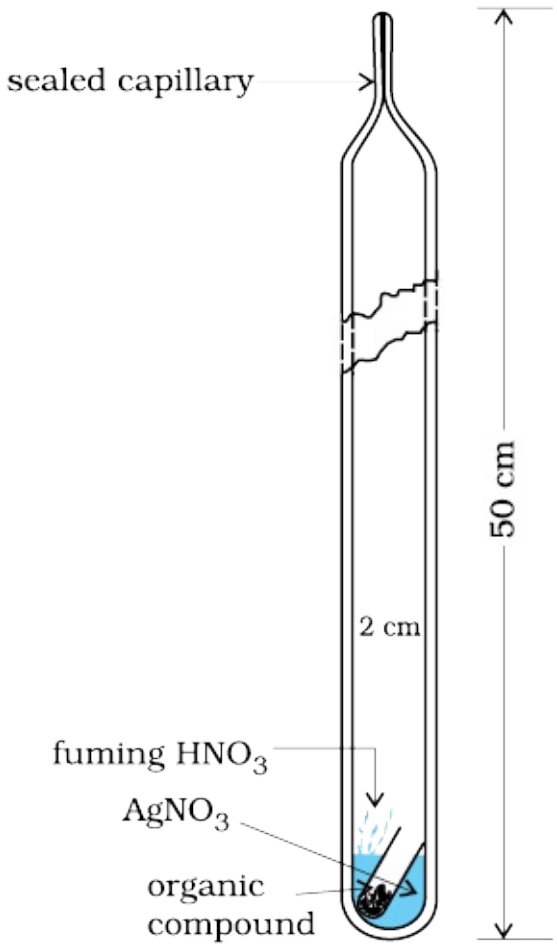


Fig.12.17 Carius method. Halogen containing organic compound is heated with fuming nitric acid in the presence of silver nitrate.

in a furnace. Carbon and hydrogen present in the compound are oxidised to carbon dioxide and water. The halogen present forms the corresponding silver halide (AgX). It is filtered, washed, dried and weighed.

Let the mass of organic

compound taken = m g

Mass of AgX formed = m1 g

1 mol of AgX contains 1 mol of X

Mass of halogen in m1g of AgX

$$= \frac{\text{atomic mass of X} \times m_1 \text{g}}{\text{molecular mass of AgX}}$$

Percentage of halogen

$$= \frac{\text{atomic mass of X} \times m_1 \times 100}{\text{molecular mass of AgX} \times m}$$

Problem 12.23

In Carius method of estimation of halogen, 0.15 g of an organic compound gave 0.12 g of AgBr. Find out the percentage of bromine in the compound.

Solution

Molar mass of AgBr = 108 + 80
= 188 g mol-1

188 g AgBr contains 80 g bromine

0.12 g AgBr contains $\frac{80 \times 0.12}{188}$ g bromine

$$\text{Percentage of bromine} = \frac{80 \times 0.12 \times 100}{188 \times 0.15}$$
$$= 34.04\%$$

12.10.4 Sulphur

A known mass of an organic compound is heated in a Carius tube with sodium peroxide or fuming nitric acid. Sulphur present in the compound is oxidised to sulphuric acid. It is precipitated as barium sulphate by adding excess of barium chloride solution in water. The precipitate is filtered, washed, dried and weighed. The percentage of sulphur can be

calculated from the mass of barium sulphate.

Let the mass of organic

compound taken = m g

and the mass of barium

sulphate formed = m1g

1 mol of $BaSO_4$ = 233 g $BaSO_4$ = 32 g sulphur

m1 g $BaSO_4$ contains $\frac{32 \times m_1}{233}$ g sulphur

$$\text{Percentage of sulphur} = \frac{32 \times m_1 \times 100}{233 \times m}$$

Problem 12.24

In sulphur estimation, 0.157 g of an organic compound gave 0.4813 g of barium sulphate. What is the percentage of sulphur in the compound?

Solution

Molecular mass of BaSO4 = 137+32+64

= 233 g

233 g BaSO4 contains 32 g sulphur

0.4813 g BaSO4 contains $\frac{32 \times 0.4813}{233}$ g sulphur

$$\text{Percentage of sulphur} = \frac{32 \times 0.4813 \times 100}{233 \times 0.157}$$
$$= 42.10\%$$

12.10.5 Phosphorus

A known mass of an organic compound is heated with fuming nitric acid whereupon phosphorus present in the compound is oxidised to phosphoric acid. It is precipitated as ammonium phosphomolybdate, $(NH_4)_3\ PO_4.12MoO_3$, by adding ammonia and ammonium molybdate. Alternatively, phosphoric acid may be precipitated as $MgNH_4PO_4$ by adding magnesia mixture which on ignition yields $Mg_2P_2O_7$.

Let the mass of organic compound taken
= m g and mass of ammonium phospho molydate = m1g

Molar mass of $(NH_4)_3PO_4.12MoO3$ = 1877g

Percentage of phosphorus = $\frac{31 \times m_1 \times 100}{1877 \times m}$ %

If phosphorus is estimated as Mg2P2O7,

Percentage of phosphorus = $\frac{62 \times m_1 \times 100}{222 \times m}$ %

where, 222 u is the molar mass of $Mg_2P_2O_7$, m, the mass of organic compound taken, m1, the mass of Mg2P2O7 formed and 62, the mass of two phosphorus atoms present in the compound $Mg_2P_2O_7$.

12.10.6 Oxygen

The percentage of oxygen in an organic compound is usually found by difference between the total percentage composition (100) and the sum of the percentages of all other elements. However, oxygen can also be estimated directly as follows:

A definite mass of an organic compound is decomposed by heating in a

stream of nitrogen gas. The mixture of gaseous products containing oxygen is passed over red-hot coke when all the oxygen is converted to carbon monoxide. This mixture is passed through warm iodine pentoxide (I_2O_5) when carbon monoxide is oxidised to carbon dioxide producing iodine.

Compound $\xrightarrow{\text{heat}}$ O_2 + other gaseous products

$2C + O_2 \xrightarrow{1373\,K} 2CO]\times 5$ (A)

$I_2O_5 + 5CO \longrightarrow I_2 + 5CO_2]\times 2$ (B)

On making the amount of CO produced in equation (A) equal to the amount of CO used in equation (B) by multiplying the equations (A) and (B) by 5 and 2 respectively; we find that each mole of oxygen liberated from the compound will produce two moles of carbondioxide.

Thus 88 g carbon dioxide is obtained if 32 g oxygen is liberated.

Let the mass of organic compound taken be m g

Mass of carbon dioxide produced be m1 g

∴ m1 g carbon dioxide is obtained from $\frac{32 \times m_1}{88}$ g O2

∴Percentage of oxygen = $\frac{32 \times m_1 \times 100}{88 \times m}$ %

The percentage of oxygen can be derived from the amount of iodine produced also.

Presently, the estimation of elements in an organic compound is carried out by using microquantities of substances and automatic experimental techniques. The elements, carbon, hydrogen and nitrogen present in a

compound are determined by an apparatus known as CHN elemental analyser. The analyser requires only a very small amount of the substance (1-3 mg) and displays the values on a screen within a short time. A detailed discussion of such methods is beyond the scope of this book.

Summary

In this unit, we have learnt some basic concepts in structure and reactivity of organic compounds, which are formed due to covalent bonding. The nature of the covalent bonding in organic compounds can be described in terms of **orbitals hybridisation** concept, according to which carbon can have sp^3, sp^2 and sp hybridised orbitals. The sp^3, sp^2 and sp hybridised carbons are found in compounds like methane, ethene and ethyne respectively. The tetrahedral shape of methane, planar shape of ethene and linear shape of ethyne can be understood on the basis of this concept. A sp^3 hybrid orbital can overlap with 1s orbital of hydrogen to give a carbon - hydrogen (C–H) single bond (sigma, σ bond). Overlap of a sp^2 orbital of one carbon with sp^2 orbital of another results in the formation of a carbon–carbon σ bond. The unhybridised p orbitals on two adjacent carbons can undergo lateral (side-by-side) overlap to give a pi (π) bond. Organic compounds can be represented by various structural formulas. The three dimensional representation of organic compounds on paper can be drawn by **wedge** and **dash** formula.

Organic compounds can be classified on the basis of their structure or the functional groups they contain. A **functional group** is an atom or group of atoms bonded together in a unique fashion and which determines the physical and chemical properties of the compounds. The naming of the organic compounds is carried out by following a set of rules laid down by the International Union of Pure and Applied Chemistry (**IUPAC**). In IUPAC nomenclature, the names are

correlated with the structure in such a way that the reader can deduce the structure from the name.

Organic reaction mechanism concepts are based on the structure of the substrate molecule, fission of a covalent bond, the attacking reagents, the electron displacement effects and the conditions of the reaction. These organic reactions involve breaking and making of covalent bonds. A covalent bond may be cleaved in **heterolytic** or **homolytic** fashion. A heterolytic cleavage yields **carbocations** or **carbanions**, while a homolytic cleavage gives **free radicals** as reactive intermediate. Reactions proceeding through heterolytic cleavage involve the complimentary pairs of reactive species. These are electron pair donor known as **nucleophile** and an electron pair acceptor known as **electrophile**. The **inductive, resonance, electromeric** and **hyperconjugation effects** may help in the polarisation of a bond making certain carbon atom or other atom positions as places of low or high electron densities.

Organic reactions can be broadly classified into following types; **substitution, addition, elimination** and **rearrangement** reactions.

Purification, qualitative and quantitative analysis of organic compounds are carried out for determining their structures. The methods of purification namely : sublimation, distillation and differential extraction are based on the difference in one or more physical properties. **Chromatography** is a useful technique of separation, identification and purification of compounds. It is classified into two categories : adsorption and partition chromatography. Adsorption chromatography is based on differential adsorption of various components of a mixture on an adsorbent. Partition chromatography involves continuous partitioning of the components of a mixture between stationary and mobile phases. After getting the compound in a pure form, its qualitative analysis is carried out for detection of elements present in it. Nitrogen, sulphur, halogens and phosphorus are detected by **Lassaigne's test**. Carbon and hydrogen are estimated by determining the amounts of carbon dioxide and water produced. Nitrogen is estimated by **Dumas** or **Kjeldahl's** method and halogens by **Carius** method. Sulphur and phosphorus are estimated by oxidising them to sulphuric and

phosphoric acids respectively. The percentage of oxygen is usually determined by difference between the total percentage (100) and the sum of percentages of all other elements present.

Exercises

12.1 What are hybridisation states of each carbon atom in the following compounds ?

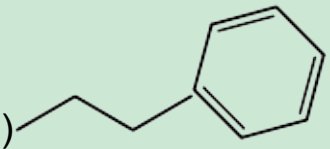
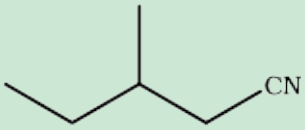
$CH_2=C=O$, $CH_3CH=CH_2$, $(CH_3)_2CO$, $CH_2=CHCN$, C_6H_6

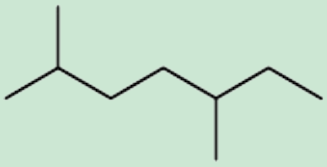
12.2 Indicate the σ and π bonds in the following molecules :

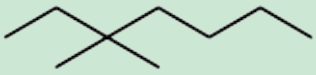
C_6H_6, C_6H_{12}, CH_2Cl_2, CH2=C=CH_2, CH_3NO_2, $HCONHCH_3$

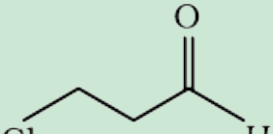
12.3 Write bond line formulas for : Isopropyl alcohol, 2,3-Dimethylbutanal, Heptan-4-one.

12.4 Give the IUPAC names of the following compounds :

(a)  (b) 

(c) 

(d) 

(e) 

(f) Cl2CHCH2OH

12.5 Which of the following represents the correct IUPAC name for the compounds
concerned ? (a) 2,2-Dimethylpentane or 2-Dimethylpentane (b) 2,4,7-Trimethyloctane or 2,5,7-Trimethyloctane (c) 2-Chloro-4-methylpentane or
4-Chloro-2-methylpentane (d) But-3-yn-1-ol or But-4-ol-1-yne.

12.6 Draw formulas for the first five members of each homologous series beginning with the following compounds. (a) H–COOH (b) CH_3COCH_3 (c) H–$CH=CH_2$

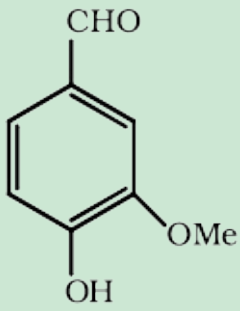
12.7 Give condensed and bond line structural formulas and identify the functional group(s) present, if any, for :

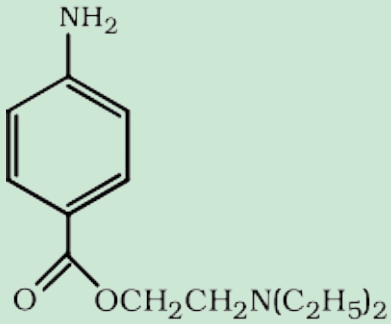
(a) 2,2,4-Trimethylpentane

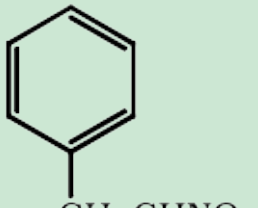
(b) 2-Hydroxy-1,2,3-propanetricarboxylic acid

(c) Hexanedial

12.8 Identify the functional groups in the following compounds

(a) 

(b) 

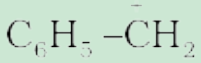
(c) 

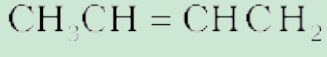
12.9 Which of the two: $O_2NCH_2CH_2O–$ or $CH_3CH_2O–$ is expected to be more stable and why ?

12.10 Explain why alkyl groups act as electron donors when attached to a π system.

12.11 Draw the resonance structures for the following compounds. Show the electron shift using curved-arrow notation.

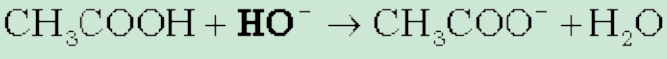
(a) C_6H_5OH (b) $C_6H_5NO_2$ (c) $CH_3CH=CHCHO$ (d) $C_6H_5–CHO$ (e)

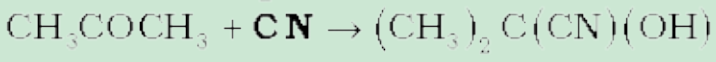


(f) 

12.12 What are electrophiles and nucleophiles ? Explain with examples.

12.13 Identify the reagents shown in bold in the following equations as nucleophiles or electrophiles:

(a) 

(b) 

(c) $C_6H_6 - \mathbf{CH_3}\overset{+}{\mathbf{C}}\mathbf{O} \rightarrow C_6H_5COCH_3$

12.14 Classify the following reactions in one of the reaction type studied in this unit.

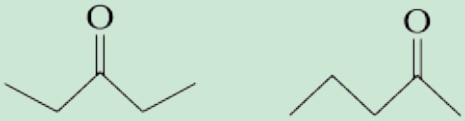
(a) $CH_3CH_2Br + HS^- \rightarrow CH_3CH_2SH + Br^-$

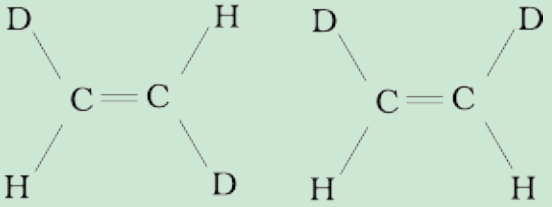
(b) $(CH_3)_2C = CH_2 + HCl \rightarrow (CH_3)_2ClC - CH_3$

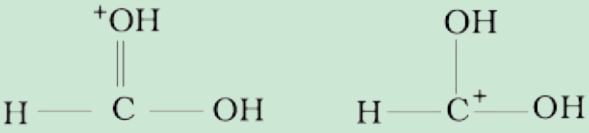
(c) $CH_3CH_2Br + HO^- \rightarrow CH_2 = CH_2 + H_2O + Br^-$

(d) $(CH_3)_3$ C - CH_2OH + BHr → $(CH_3)_2$ $CBrCH_2CH_2CH_3$ + H_2O

12.15 What is the relationship between the members of following pairs of structures ? Are they structural or geometrical isomers or resonance contributors ?

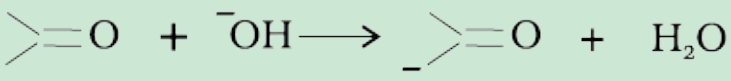
(a) 

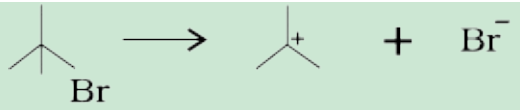
(b) 

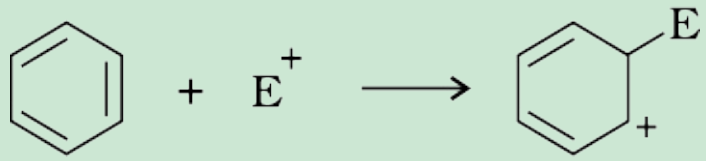
(c) 

12.16 For the following bond cleavages, use curved-arrows to show the electron flow and classify each as homolysis or heterolysis. Identify reactive intermediate produced as free radical, carbocation and carbanion.

(a) $CH_3O - OCH_3 \rightarrow CH_3\dot{O} + \dot{O}CH_3$

(b) 

(c) 

(d) 

12.17 Explain the terms Inductive and Electromeric effects. Which electron displacement effect explains the following correct orders of acidity of the carboxylic acids?

(a) $Cl_3CCOOH > Cl_2CHCOOH > ClCH_2COOH$

(b) $CH_3CH_2COOH > (CH_3)_2CHCOOH > (CH_3)_3C.COOH$

12.18 Give a brief description of the principles of the following techniques taking an example in each case.

(a) Crystallisation (b) Distillation (c) Chromatography

12.19 Describe the method, which can be used to separate two compounds with different solubilities in a solvent S.

12.20 What is the difference between distillation, distillation under reduced pressure and steam distillation ?

12.21 Discuss the chemistry of Lassaigne's test.

12.22 Differentiate between the principle of estimation of nitrogen in an organic compound by (i) Dumas method and (ii) Kjeldahl's method.

12.23 Discuss the principle of estimation of halogens, sulphur and phosphorus present in an organic compound.

12.24 Explain the principle of paper chromatography.

12.25 Why is nitric acid added to sodium extract before adding silver nitrate for testing halogens?

12.26 Explain the reason for the fusion of an organic compound with metallic sodium for testing nitrogen, sulphur and halogens.

12.27 Name a suitable technique of separation of the components

from a mixture of calcium sulphate and camphor.

12.28 Explain, why an organic liquid vaporises at a temperature below its boiling point in its steam distillation ?

12.29 Will CCl4 give white precipitate of AgCl on heating it with silver nitrate? Give reason for your answer.

12.30 Why is a solution of potassium hydroxide used to absorb carbon dioxide evolved during the estimation of carbon present in an organic compound?

12.31 Why is it necessary to use acetic acid and not sulphuric acid for acidification of sodium extract for testing sulphur by lead acetate test?

12.32 An organic compound contains 69% carbon and 4.8% hydrogen, the remainder being oxygen. Calculate the masses of carbon dioxide and water produced when 0.20 g of this substance is subjected to complete combustion.

12.33 A sample of 0.50 g of an organic compound was treated according to Kjeldahl's method. The ammonia evolved was absorbed in 50 ml of 0.5 M H_2SO_4. The residual acid required 60 mL of 0.5 M solution of NaOH for neutralisation. Find the percentage composition of nitrogen in the compound.

12.34 0.3780 g of an organic chloro compound gave 0.5740 g of silver chloride in Carius estimation. Calculate the percentage of chlorine present in the compound.

12.35 In the estimation of sulphur by Carius method, 0.468 g of an organic sulphur compound afforded 0.668 g of barium sulphate. Find out the percentage of sulphur in the given compound.

12.36 In the organic compound $CH_2 = CH - CH_2 - CH_2 - C \equiv CH$, the pair of hydridised orbitals involved in the formation of: $C_2 - C_3$ bond is:

(a) $sp - sp^2$ (b) $sp - sp^3$ (c) $sp^2 - sp^3$ (d) $sp^3 - sp^3$

12.37 In the Lassaigne's test for nitrogen in an organic compound, the Prussian blue colour is obtained due to the formation of:

(a) $Na_4[Fe(CN)_6]$ (b) $Fe_4[Fe(CN)_6]_3$ (c) $Fe_2[Fe(CN)_6]$ (d) $Fe_3[Fe(CN)_6]_4$

12.38 Which of the following carbocation is most stable ?

(a) $(CH_3)_3C.\overset{+}{C}H_2$ (b) $(CH_3)_3\overset{+}{C}$ (c) $CH_3CH_2\overset{+}{C}H_2$ (d) $CH_3\overset{+}{C}HCH_2CH_3$

12.39 The best and latest technique for isolation, purification and separation of organic compounds is:

(a) Crystallisation (b) Distillation (c) Sublimation (d) Chromatography

12.40 The reaction:

$CH_3CH_2I + KOH(aq) \rightarrow CH_3CH_2OH + KI$

is classified as :

(a) electrophilic substitution (b) nucleophilic substitution

(c) elimination (d) addition

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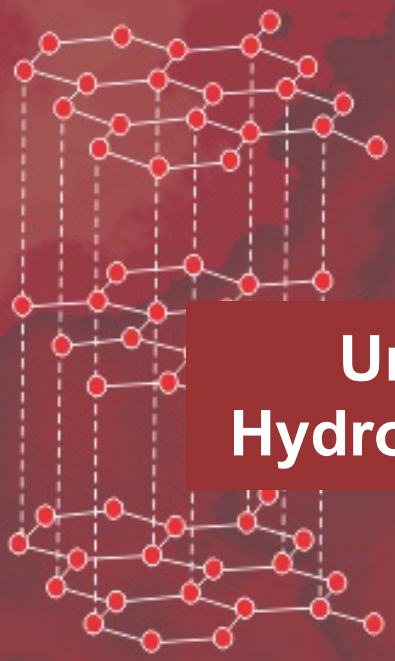
(A) Test for Nitrogen
(B) Test for Sulphur

(C) Test for Halogens

(D) Test for Phosphorus

12.10 Quantitative Analysis
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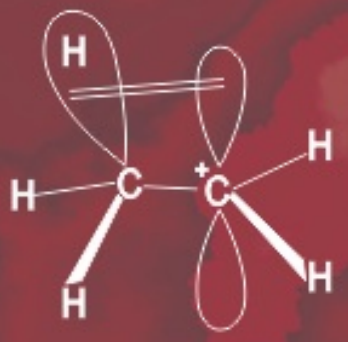
Textbook for Class XI



Unit 13
Hydrocarbons

Chemistry

Part II



11083CH13

Unit 13

Hydrocarbons

Objectives

After studying this unit, you will be able to

• name hydrocarbons according to IUPAC system of nomenclature;

• recognise and write structures of isomers of alkanes, alkenes, alkynes and aromatic hydrocarbons;

• learn about various methods of preparation of hydrocarbons;

• distinguish between alkanes, alkenes, alkynes and aromatic hydrocarbons on the basis of physical and chemical properties;

• draw and differentiate between various conformations of ethane;

• appreciate the role of hydrocarbons as sources of energy and for other industrial applications;

• predict the formation of the addition products of unsymmetrical alkenes and alkynes on the basis of electronic mechanism;

- comprehend the structure of benzene, explain aromaticity and understand mechanism of electrophilic substitution reactions of benzene;
- predict the directive influence of substituents in monosubstituted benzene ring;
- learn about carcinogenicity and toxicity.

*"**Hydrocarbons are the important sources of energy.**"*

The term 'hydrocarbon' is self-explanatory which means compounds of carbon and hydrogen only. Hydrocarbons play a key role in our daily life. You must be familiar with the terms 'LPG' and 'CNG' used as fuels. LPG is the abbreviated form of liquified petroleum gas whereas CNG stands for compressed natural gas. Another term 'LNG' (liquified natural gas) is also in news these days. This is also a fuel and is obtained by liquifaction of natural gas. Petrol, diesel and kerosene oil are obtained by the fractional distillation of petroleum found under the earth's crust.

Coal gas is obtained by the destructive distillation of coal. Natural gas is found in upper strata during drilling of oil wells. The gas after compression is known as compressed natural gas. LPG is used as a domestic fuel with the least pollution. Kerosene oil is also used as a domestic fuel but it causes some pollution. Automobiles need fuels like petrol, diesel and CNG. Petrol and CNG operated automobiles cause less pollution. All these fuels contain mixture of hydrocarbons, which are sources of energy. Hydrocarbons are also used for the manufacture of polymers like polythene, polypropene, polystyrene etc. Higher hydrocarbons are used as solvents for paints. They are also used as the starting materials for manufacture of many dyes and drugs. Thus, you can well understand the importance of hydrocarbons in your daily life. In this unit, you will learn more about hydrocarbons.

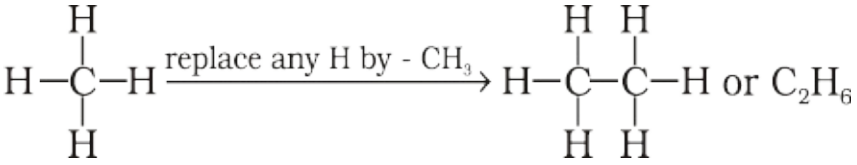
13.1 CLASSIFICATION

Hydrocarbons are of different types. Depending upon the types of carbon-carbon bonds present, they can be classified into three main categories – (i) saturated
(ii) unsaturated and (iii) aromatic hydrocarbons. Saturated hydrocarbons contain carbon-carbon and carbon-hydrogen single bonds. If different carbon atoms are joined together to form open chain of carbon atoms with single bonds, they are termed as alkanes as you have already studied in Unit 12. On the other hand, if carbon atoms form a closed chain or a ring, they are termed as cycloalkanes. Unsaturated hydrocarbons contain carbon-carbon multiple bonds – double bonds, triple bonds or both. Aromatic hydrocarbons are a special type of cyclic compounds. You can construct a large number of models of such molecules of both types (open chain and close chain) keeping in mind that carbon is tetravalent and hydrogen is monovalent. For making models of alkanes, you can use toothpicks for bonds and plasticine balls for atoms. For alkenes, alkynes and aromatic hydrocarbons, spring models can be constructed.

13.2 ALKANES

As already mentioned, alkanes are saturated open chain hydrocarbons containing carbon - carbon single bonds. Methane (CH_4) is the first member of this family. Methane is a gas found in coal mines and marshy places. If you replace one hydrogen atom of methane by carbon and join the required number of hydrogens to satisfy the tetravalence of the other carbon atom, what do you get? You get C_2H_6. This hydrocarbon with molecular formula C_2H_6 is known as ethane. Thus you can consider C_2H_6 as derived from CH4 by replacing one hydrogen atom by $-CH_3$

group. Go on constructing alkanes by doing this theoretical exercise i.e., replacing hydrogen atom by $-CH_3$ group. The next molecules will be C_3H_8, C_4H_{10} ...



These hydrocarbons are inert under normal conditions as they do not react with acids, bases and other reagents. Hence, they were earlier known as paraffins (latin : parum, little; affinis, affinity). Can you think of the general formula for alkane family or **homologous series**? If we examine the formula of different alkanes we find that the general formula for alkanes is C_nH_{2n+2}. It represents any particular homologue when n is given appropriate value. Can you recall the structure of methane? According to VSEPR theory (Unit 4), methane has a tetrahedral structure (Fig. 13.1), in which carbon atom lies at the centre and the four hydrogen atoms lie at the four corners of a regular tetrahedron. All H-C-H bond angles are of 109.5°.

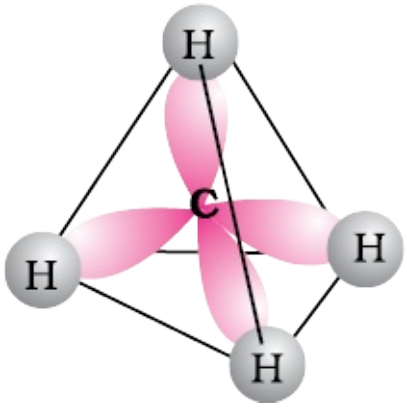


Fig. 13.1 Structure of methane

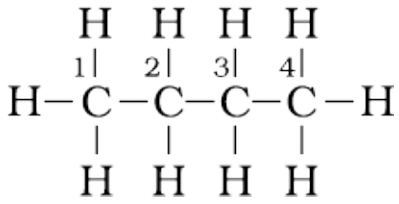
In alkanes, tetrahedra are joined together in which C-C and C-H bond lengths are 154 pm and 112 pm respectively (Unit 12). You have already

read that C–C and C–H σ bonds are formed by head-on overlapping of sp3 hybrid orbitals of carbon and 1s orbitals of hydrogen atoms.

13.2.1 Nomenclature and Isomerism

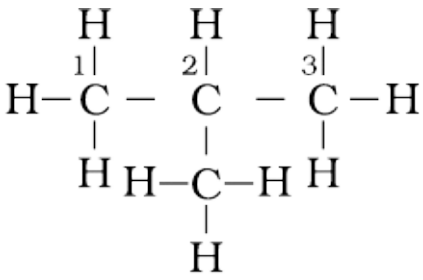
You have already read about nomenclature of different classes of organic compounds in Unit 12. Nomenclature and isomerism in alkanes can further be understood with the help of a few more examples. Common names are given in parenthesis. First three alkanes – methane, ethane and propane have only one structure but higher alkanes can have more than one structure. Let us write structures for C_4H_{10}. Four carbon atoms of C_4H_{10} can be joined either in a continuous chain or with a branched chain in the following two ways :

I



Butane (n- butane), (b.p. 273 K)

II

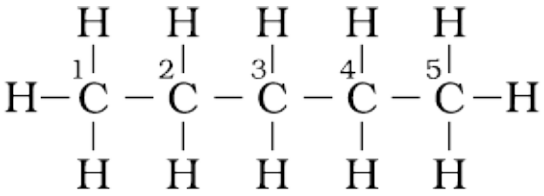


2-Methylpropane (isobutane) (b.p.261 K)

In how many ways, you can join five carbon atoms and twelve hydrogen atoms of C_5H_{12}? They can be arranged in three ways as shown in

structures III–V

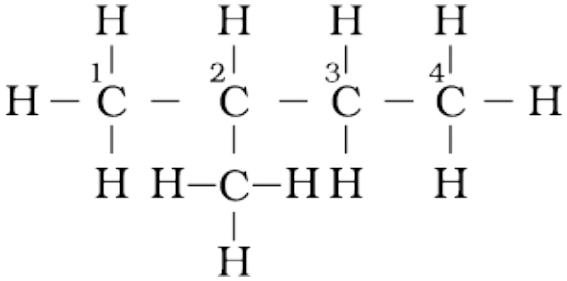
III



Pentane (n-pentane)

(b.p. 309 K)

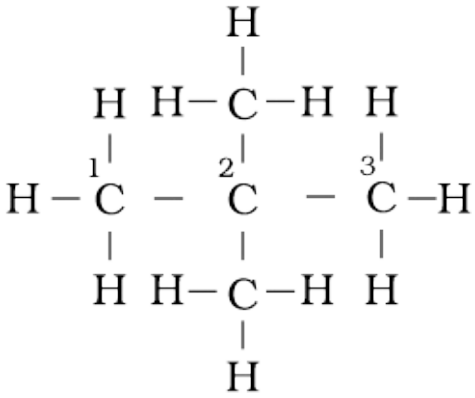
IV



2-Methylbutane (isopentane)

(b.p. 301 K)

V



2,2-Dimethylpropane (neopentane)

(b.p. 282.5 K)

Structures I and II possess same molecular formula but differ in their boiling points and other properties. Similarly structures III, IV and V possess the same molecular formula but have different properties. Structures I and II are isomers of butane, whereas structures III, IV and V are isomers of pentane. Since difference in properties is due to difference in their structures, they are known as **structural isomers**. It is also clear that structures I and III have continuous chain of carbon atoms but structures II, IV and V have a branched chain. Such structural isomers which differ in chain of carbon atoms are known as **chain isomers**. Thus, you have seen that C_4H_{10} and C_5H_{12} have two and three chain isomers respectively.

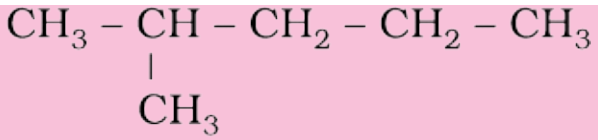
Problem 13.1

Write structures of different chain isomers of alkanes corresponding to the molecular formula C_6H_{14}. Also write their IUPAC names.

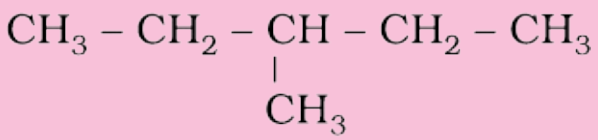
Solution

(i) $CH_3 – CH_2 – CH_2 – CH_2– CH_2– CH_3$

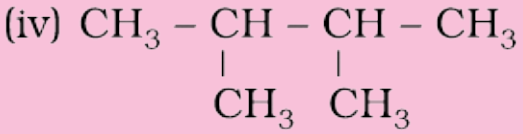
n-Hexane

(ii) 

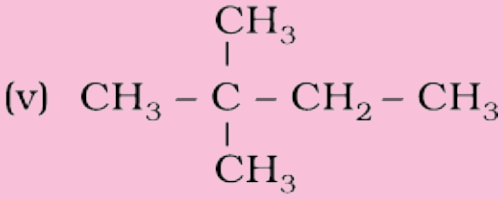
2-Methylpentane

(iii) 

3-Methylpentane

(iv) 

2,3-Dimethylbutane

(v) 

2,2 - Dimethylbutane

Based upon the number of carbon atoms attached to a carbon atom, the carbon atom is termed as primary (1°), secondary (2°), tertiary (3°) or quaternary (4°). Carbon atom attached to no other carbon atom as in methane or to only one carbon atom as in ethane is called primary carbon atom. Terminal carbon atoms are always primary. Carbon atom attached to two carbon atoms is known as secondary. Tertiary carbon is attached to three carbon atoms and neo or quaternary carbon is attached to four carbon atoms. Can you identify 1°, 2°, 3° and 4° carbon atoms in structures I to V ? If you go on constructing structures for higher alkanes,

you will be getting still larger number of isomers. C_6H_{14} has got five isomers and C_7H_{16} has nine. As many as 75 isomers are possible for $C_{10}H_{22}$.

In structures II, IV and V, you observed that $–CH_3$ group is attached to carbon atom numbered as 2. You will come across groups like $–CH_3$, $–C_2H_5$, $–C_3H_7$ etc. attached to carbon atoms in alkanes or other classes of compounds. These groups or substituents are known as alkyl groups as they are derived from alkanes by removal of one hydrogen atom. General formula for alkyl groups is C_nH_{2n+1} (Unit 12).

Let us recall the general rules for nomenclature already discussed in Unit 12. Nomenclature of substituted alkanes can further be understood by considering the following problem:

Problem 13.2

Write structures of different isomeric alkyl groups corresponding to the molecular formula C_5H_{11}. Write IUPAC names of alcohols obtained by attachment of –OH groups at different carbons of the chain.

Solution

Structures of – C_5H_{11} group	Corresponding alcohols	Name of alcohol
(i) $CH_3 - CH_2 - CH_2 - CH_2 - CH_2 -$	$CH_3 - CH_2 - CH_2 - CH_2 - CH_2 - OH$	Pentan-1-ol
(ii) $CH_3 - \underset{\displaystyle |}{CH} - CH_2 - CH_2 - CH_3$	$CH_3 - \underset{\displaystyle OH}{\underset{\displaystyle |}{CH}} - CH_2 - CH_2 - CH_3$	Pentan-2-ol
(iii) $CH_3 - CH_2 - \underset{\displaystyle |}{CH} - CH_2 - CH_3$	$CH_3 - CH_2 - \underset{\displaystyle OH}{\underset{\displaystyle |}{CH}} - CH_2 - CH_3$	Pentan-3-ol
(iv) $\underset{\displaystyle CH_3}{\underset{\displaystyle |}{}}$ $CH_3 - CH - CH_2 - CH_2 -$	$\underset{\displaystyle CH_3}{\underset{\displaystyle |}{}}$ $CH_3 - CH - CH_2 - CH_2 - OH$	3-Methyl-butan-1-ol
(v) $\underset{\displaystyle CH_3}{\underset{\displaystyle |}{}}$ $CH_3 - CH_2 - CH - CH_2 -$	$\underset{\displaystyle CH_3}{\underset{\displaystyle |}{}}$ $CH_3 - CH_2 - CH - CH_2 - OH$	2-Methyl-butan-1-ol
(vi) $\underset{\displaystyle CH_3}{\underset{\displaystyle |}{}}$ $CH_3 - C - CH_2 - CH_3$	$\underset{\displaystyle CH_3}{\underset{\displaystyle |}{}}$ $CH_3 - C - CH_2 - CH_3$ $\underset{\displaystyle OH}{\underset{\displaystyle |}{}}$	2-Methyl-butan-2-ol
(vii) $\underset{\displaystyle CH_3}{\underset{\displaystyle |}{}}$ $CH_3 - C - CH_2 -$ $\underset{\displaystyle CH_3}{\underset{\displaystyle |}{}}$	$\underset{\displaystyle CH_3}{\underset{\displaystyle |}{}}$ $CH_3 - C - CH_2OH$ $\underset{\displaystyle CH_3}{\underset{\displaystyle |}{}}$	2,2- Dimethyl-propan-1-ol
(viii) $\underset{\displaystyle CH_3}{\underset{\displaystyle |}{}}$ $\quad\underset{\displaystyle |}{}$ $CH_3 - CH - CH - CH_3$	$\underset{\displaystyle CH_3}{\underset{\displaystyle |}{}}$ $\quad\underset{\displaystyle OH}{\underset{\displaystyle |}{}}$ $CH_3 - CH - CH - CH_3$	3-Methyl-butan-2-ol

Structures of – C_5H_{11} group Corresponding alcohols Name of alcohol

(i) CH3 – CH2 – CH2 – CH2– CH2 – CH3 – CH2 – CH2 – CH2– CH2 – OH Pentan-1-ol

(ii) CH3 – CH – CH2 – CH2 – CH3 CH3 – CH – CH2 – CH2– CH3 Pentan-2-ol

| |

OH

(iii) CH3 – CH2 – CH – CH2 – CH3 CH3 – CH2 – CH – CH2– CH3 Pentan-3-ol

| |

OH

CH3 CH3 3-Methyl-
| | butan-1-ol

(iv) CH3 – CH – CH2 – CH2 – CH3 – CH – CH2 – CH2– OH

CH3 CH3 2-Methyl-
| | butan-1-ol

(v) CH3 – CH2 – CH – CH2 – CH3 – CH2 – CH – CH2– OH

CH3 CH3 2-Methyl-
| | butan-2-ol

(vi) CH3 – C – CH2 – CH3 CH3 – C – CH2 – CH3

| |

OH

CH3 CH3 2,2- Dimethyl-
| | propan-1-ol

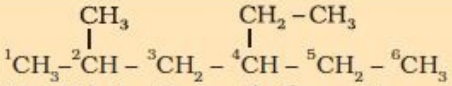
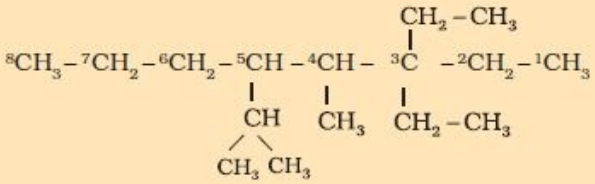
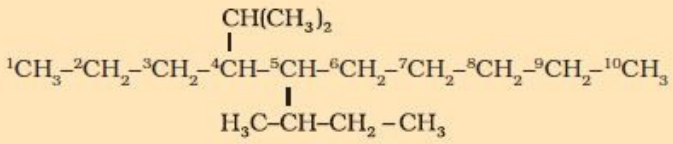
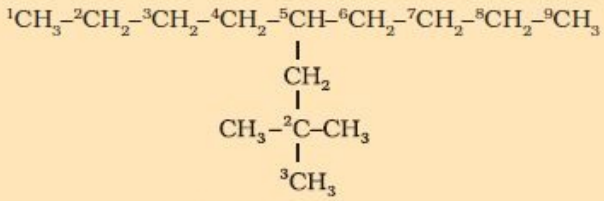
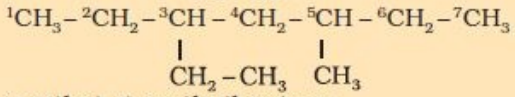
(vii) CH3 – C – CH2 – CH3 – C – CH2OH

| |

CH3 CH3

CH3 CH3 OH 3-Methyl- | | | | butan-2-ol
(viii) CH3 – CH – CH –CH3 CH3 – CH – CH –CH3

Table 13.1 Nomenclature of a Few Organic Compounds

Structure and IUPAC Name	Remarks
(a)  (4 – Ethyl – 2 – methylhexane)	Lowest sum and alphabetical arrangement
(b)  (3,3-Diethyl-5-isopropyl-4-methyloctane)	Lowest sum and alphabetical arrangement
(c)  5-*sec*– Butyl-4-isopropyldecane	*sec* is not considered while arranging alphabetically; isopropyl is taken as one word
(d)  5-(2,2– Dimethylpropyl)nonane	Further numbering to the substituents of the side chain
(e)  3–Ethyl–5–methylheptane	Alphabetical priority order

Problem 13.3

Write IUPAC names of the following compounds :

(i) (CH3)3 C CH2C(CH3)3

(ii) (CH3)2 C(C2H5)2

(iii) tetra – tert-butylmethane

Solution

(i) 2, 2, 4, 4-Tetramethylpentane

(ii) 3, 3-Dimethylpentane

(iii) 3,3-Di-tert-butyl -2, 2, 4, 4 - tetramethylpentane

If it is important to write the correct IUPAC name for a given structure, it is equally important to write the correct structure from the given IUPAC name. To do this, first of all, the longest chain of carbon atoms corresponding to the parent alkane is written. Then after numbering it, the substituents are attached to the correct carbon atoms and finally valence of each carbon atom is satisfied by putting the correct number of hydrogen atoms. This can be clarified by writing the structure of 3-ethyl-2, 2–dimethylpentane in the following steps :

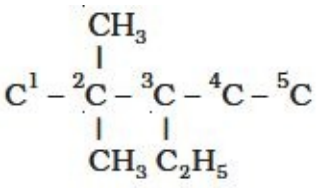
i) Draw the chain of five carbon atoms:

C – C – C – C – C

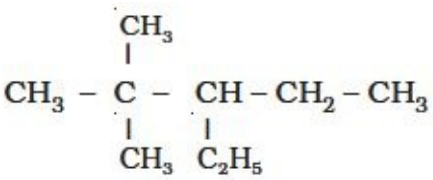
ii) Give number to carbon atoms:

$C^1 – C^2 – C^3 – C^4 – C^5$

iii) Attach ethyl group at carbon 3 and two methyl groups at carbon 2



iv) Satisfy the valence of each carbon atom by putting requisite number of hydrogen atoms :



Thus we arrive at the correct structure. If you have understood writing of structure from the given name, attempt the following problems.

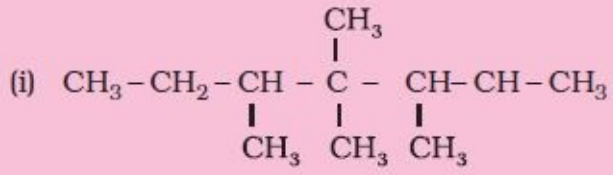
Problem 13.4

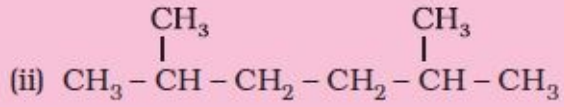
Write structural formulas of the following compounds :

(i) 3, 4, 4, 5–Tetramethylheptane

(ii) 2,5-Dimethyhexane

Solution





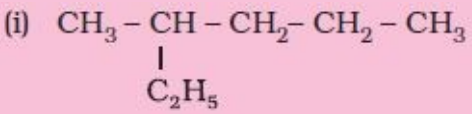
Problem 13.5

Write structures for each of the following compounds. Why are the given names incorrect? Write correct IUPAC
names.

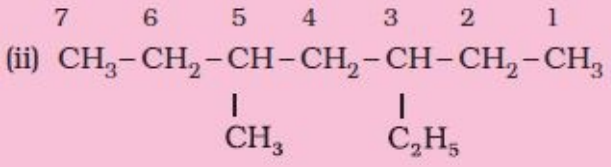
(i) 2-Ethylpentane

(ii) 5-Ethyl – 3-methylheptane

Solution



Longest chain is of six carbon atoms and not that of five. Hence, correct name is
3-Methylhexane.

(ii) 

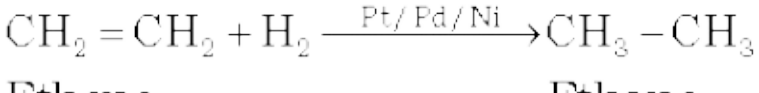
Numbering is to be started from the end which gives lower number to ethyl group. Hence, correct name is 3-ethyl-5-methylheptane.

13.2.2 Preparation

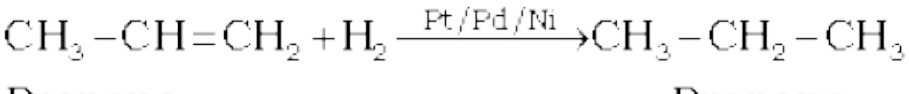
Petroleum and natural gas are the main sources of alkanes. However, alkanes can be prepared by following methods :

1. From unsaturated hydrocarbons

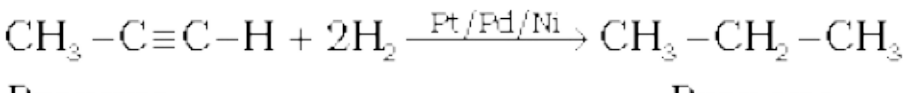
Dihydrogen gas adds to alkenes and alkynes in the presence of finely divided catalysts like platinum, palladium or nickel to form alkanes. This process is called **hydrogenation**. These metals adsorb dihydrogen gas on their surfaces and activate the hydrogen – hydrogen bond. Platinum and palladium catalyse the reaction at room temperature but relatively higher temperature and pressure are required with nickel catalysts.



Ethene Ethane (13.1)



Propene Propane (13.2)



Propyne Propane (13.3)

2. From alkyl halides

i) Alkyl halides (except fluorides) on reduction with zinc and dilute hydrochloric acid give alkanes.

$$CH_3-Cl + H_2 \xrightarrow{Zn,\ H^+} CH_4 + HCl \quad (13.4)$$

Chloromethane Methane

$$C_2H_5-Cl + H_2 \xrightarrow{Zn,\ H^+} C_2H_6 + HCl$$

Chloroethane Ethane (13.5)

$$CH_3CH_2CH_2Cl + H_2 \xrightarrow{Zn,H^+} CH_3CH_2CH_3 + HCl$$

1-Chloropropane Propane (13.6)

ii) Alkyl halides on treatment with sodium metal in dry ethereal (free from moisture) solution give higher alkanes. This reaction is known as **Wurtz reaction** and is used for the preparation of higher alkanes containing even number of carbon
atoms.

$$CH_3Br + 2Na + BrCH_3 \xrightarrow{\text{dry ether}} CH_3-CH_3 + 2NaBr$$

Bromomethane Ethane

(13.7)

$$C_2H_5Br + 2Na + BrC_2H_5 \xrightarrow{\text{dry ether}} C_2H_5-C_2H_5$$

Bromoethane n-Butane

(13.8)

What will happen if two different alkyl halides are taken?

3. From carboxylic acids

i) Sodium salts of carboxylic acids on heating with soda lime (mixture of sodium hydroxide and calcium oxide) give alkanes containing one carbon atom less than the carboxylic acid. This process of elimination of carbon dioxide from a carboxylic acid is known as **decarboxylation**.

$$CH_3COO^-Na^+ + NaOH \xrightarrow[\Delta]{CaO} CH_4 + Na_2CO_3$$

Sodium ethanoate

Problem 13.6

Sodium salt of which acid will be needed for the preparation of propane ? Write chemical equation for the reaction.

Solution

Butanoic acid,

$$CH_3CH_2CH_2COO^-Na^+ + NaOH \xrightarrow{CaO} CH_3CH_2CH_3 + Na_2CO_3$$

ii) Kolbe's electrolytic method An aqueous solution of sodium or potassium salt of a carboxylic acid on electrolysis

gives alkane containing even number of carbon atoms at the anode.

$$\underset{\text{Sodium acetate}}{2CH_3COO^-Na^+ + 2H_2O} \xrightarrow{\text{Electrolysis}} CH_3-CH_3 + 2CO_2 + H_2 + 2NaOH$$

(13.9)

The reaction is supposed to follow the following path :

i) $2CH_3COO^-Na^+ \rightleftharpoons 2CH_3-\overset{\overset{O}{\|}}{C}-O^- + 2Na^+$

ii) At anode:

$$2CH_3-\overset{\overset{O}{\|}}{C}-O^- \xrightarrow{-2e^-} 2CH_3-\overset{\overset{O}{\|}}{C}-\dot{\underset{\cdot\cdot}{O}}: \longrightarrow 2\dot{C}H_3 + 2CO_2\uparrow$$

Acetate ion Acetate free radical Methyl free radical

iii)

$$H_3\dot{C} + \dot{C}H_3 \longrightarrow H_3C-CH_3\uparrow$$

iv) At cathode :

$$H_2O + e^- \rightarrow {}^-OH + \dot{H}$$

$$2\dot{H} \rightarrow H_2\uparrow$$

Methane cannot be prepared by this method. Why?

13.2.3 Properties

Physical properties

Alkanes are almost non-polar molecules because of the covalent nature of C-C and C-H bonds and due to very little difference of electronegativity between carbon and hydrogen atoms. They possess weak van der Waals forces. Due to the weak forces, the first four members, C_1 to C_4 are gases, C_5 to C_{17} are liquids and those containing 18 carbon atoms or more are solids at 298 K. They are colourless and odourless. What do

you think about solubility of alkanes in water based upon non-polar nature of alkanes? Petrol is a mixture of hydrocarbons and is used as a fuel for automobiles. Petrol and lower fractions of petroleum are also used for dry cleaning of clothes to remove grease stains. On the basis of this observation, what do you think about the nature of the greasy substance? You are correct if you say that grease (mixture of higher alkanes) is non-polar and, hence, hydrophobic in nature. It is generally observed that in relation to solubility of substances in solvents, polar substances are soluble in polar solvents, whereas the non-polar ones in non-polar solvents i.e., like dissolves like.

Boiling point (b.p.) of different alkanes are given in Table 13.2 from which it is clear that there is a steady increase in boiling point with increase in molecular mass. This is due to the fact that the intermolecular van der Waals forces increase with increase of the molecular size or the surface area of the molecule.

You can make an interesting observation by having a look on the boiling points of three isomeric pentanes viz., (pentane,
2-methylbutane and 2,2-dimethylpropane). It is observed (Table 13.2) that pentane having a continuous chain of five carbon atoms has the highest boiling point (309.1K) whereas 2,2 – dimethylpropane boils at 282.5K. With increase in number of branched chains, the molecule attains the shape of a sphere. This results in smaller area of contact and therefore weak intermolecular forces between spherical molecules, which are overcome at relatively lower temperatures.

Chemical properties

As already mentioned, alkanes are generally inert towards acids, bases, oxidising and reducing agents. However, they undergo the following reactions under certain

conditions.

1. Substitution reactions

One or more hydrogen atoms of alkanes can be replaced by halogens, nitro group and sulphonic acid group. Halogenation takes place either at higher temperature
(573-773 K) or in the presence of diffused sunlight or ultraviolet light. Lower alkanes do not undergo nitration and sulphonation reactions. These reactions in which hydrogen atoms of alkanes are substituted are known as substitution reactions. As an example, chlorination of methane is given below:

Halogenation

$$CH_4 + Cl_2 \xrightarrow{h\nu} CH_3Cl + HCl$$

Chloromethane (13.10)

$$CH_3Cl + Cl_2 \xrightarrow{h\nu} CH_2Cl_2 + HCl$$

Dichloromethane (13.11)

$$CH_2Cl_2 + Cl_2 \xrightarrow{h\nu} CHCl_3 + HCl$$

Trichloromethane (13.12)

$$CHCl_3 + Cl_2 \xrightarrow{h\nu} CCl_4 + HCl$$

Tetrachloromethane (13.13)

Table 13.2 Variation of Melting Point and Boiling Point in Alkanes

Molecular formula	Name	Molecular mass/u	b.p./(K)	m.p./(K)
CH_4	Methane	16	111.0	90.5
C_2H_6	Ethane	30	184.4	101.0
C_3H_8	Propane	44	230.9	85.3
C_4H_{10}	Butane	58	272.4	134.6
C_4H_{10}	2-Methylpropane	58	261.0	114.7
C_5H_{12}	Pentane	72	309.1	143.3
C_5H_{12}	2-Methylbutane	72	300.9	113.1
C_5H_{12}	2,2-Dimethylpropane	72	282.5	256.4
C_6H_{14}	Hexane	86	341.9	178.5
C_7H_{16}	Heptane	100	371.4	182.4
C_8H_{18}	Octane	114	398.7	216.2
C_9H_{20}	Nonane	128	423.8	222.0
$C_{10}H_{22}$	Decane	142	447.1	243.3
$C_{20}H_{42}$	Eicosane	282	615.0	236.2

$$CH_3\text{-}CH_3 + Cl_2 \xrightarrow{h\nu} CH_3\text{–}CH_2Cl + HCl$$

Chloroethane (13.14)

It is found that the rate of reaction of alkanes with halogens is $F_2 > Cl_2 > Br_2 > I_2$. Rate of replacement of hydrogens of alkanes is : 3° > 2° > 1°. Fluorination is too violent to be controlled. Iodination is very slow and a reversible reaction. It can be carried out in the presence of oxidizing agents like HIO_3 or HNO_3.

$$CH_4 + I_2 \rightleftharpoons CH_3I + HI \quad (13.15)$$

$$HIO_3 + 5HI \rightarrow 3I_2 + 3H_2O \quad (13.16)$$

Halogenation is supposed to proceed via free radical chain mechanism involving three steps namely initiation, propagation and termination as given below:

Mechanism

(i) Initiation : The reaction is initiated by homolysis of chlorine molecule in the presence of light or heat. The Cl–Cl bond is weaker than the C–C

and C–H bond and hence, is easiest to break.

$$Cl-Cl \xrightarrow[\text{homolysis}]{h\nu} \underset{\text{Chlorine free radicals}}{\dot{Cl} \quad + \quad \dot{Cl}}$$

(ii) Propagation : Chlorine free radical attacks the methane molecule and takes the reaction in the forward direction by breaking the C-H bond to generate methyl free radical with the formation of H-Cl.

$$\text{(a) } CH_4 + \dot{Cl} \xrightarrow{h\nu} \dot{C}H_3 + H-Cl$$

The methyl radical thus obtained attacks the second molecule of chlorine to form CH_3 – Cl with the liberation of another chlorine free radical by homolysis of chlorine molecule.

$$\text{(b) } \dot{C}H_3 + Cl-Cl \xrightarrow{h\nu} \underset{\text{Chlorine free radical}}{CH_3-Cl \quad + \quad \dot{Cl}}$$

The chlorine and methyl free radicals generated above repeat steps (a) and (b) respectively and thereby setup a chain of reactions. The propagation steps (a) and (b) are those which directly give principal products, but many other propagation steps are possible and may occur. Two such steps given below explain how more highly haloginated products are formed.

$$CH_3Cl + \dot{Cl} \rightarrow \dot{C}H_2Cl + HCl$$

$$\dot{C}H_2Cl + Cl-Cl \rightarrow CH_2Cl_2 + \dot{Cl}$$

(iii) Termination: The reaction stops after some time due to consumption of reactants and / or due to the following side reactions :

The possible chain terminating steps are :

(a) $\dot{Cl} + \dot{Cl} \rightarrow Cl-Cl$

(b) $H_3\dot{C} + \dot{C}H_3 \rightarrow H_3C-CH_3$

(c) $H_3\dot{C} + \dot{Cl} \rightarrow H_3C-Cl$

Though in (c), CH3 – Cl, the one of the products is formed but free radicals are consumed and the chain is terminated. The above mechanism helps us to understand the reason for the formation of ethane as a byproduct during chlorination of methane.

2. Combustion

Alkanes on heating in the presence of air or dioxygen are completely oxidized to carbon dioxide and water with the evolution of large amount of heat.

$$CH_4(g)+2O_2(g) \rightarrow CO_2(g)+2H_2O(l); \quad \Delta_c H^{\ominus} = -890\ kJ\ mol^{-1} \qquad (13.17)$$

$$C_4H_{10}(g)+13/2\ O_2(g) \rightarrow 4CO_2(g)+5H_2O(l); \quad \Delta_c H^{\ominus} = -2875.84\ kJ\ mol^{-1}$$

(13.18)

The general combustion equation for any alkane is :

$$C_nH_{2n+2} + \left(\frac{3n+1}{2}\right)O_2 \rightarrow nCO_2 + (n+1)H_2O \qquad (13.19)$$

Due to the evolution of large amount of heat during combustion, alkanes

are used as fuels.

During incomplete combustion of alkanes with insufficient amount of air or dioxygen, carbon black is formed which is used in the manufacture of ink, printer ink, black pigments and as filters.

$$CH_4(g) + O_2(g) \xrightarrow[\text{combustion}]{\text{Incomplete}} C(s) + 2H_2O(l)$$

(13.20)

3. Controlled oxidation

Alkanes on heating with a regulated supply of dioxygen or air at high pressure and in the presence of suitable catalysts give a variety of oxidation products.

$$\text{(i)}\quad 2CH_4 + O_2 \xrightarrow{Cu/523K/100\,atm} \underset{\text{Methanol}}{2CH_3OH}$$

(13.21)

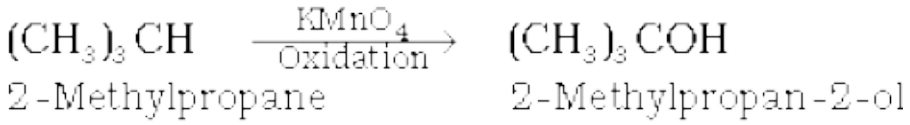
$$\text{(ii)}\quad CH_4 + O_2 \xrightarrow[\Delta]{Mo_2O_3} HCHO + H_2O$$
Methanal

(13.22)

$$\text{(iii)}\quad 2CH_3CH_3 + 3O_2 \xrightarrow[\Delta]{(CH_3COO)_2Mn} \underset{\text{Ethanoic acid}}{2CH_3COOH} + 2H_2O$$

(13.23)

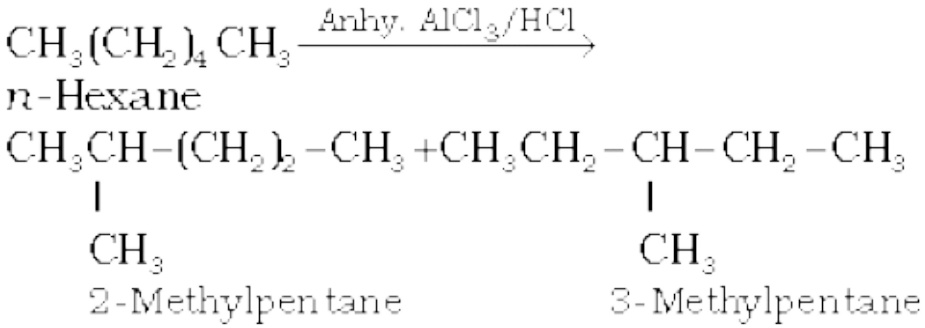
(iv) Ordinarily alkanes resist oxidation but alkanes having tertiary H atom can be oxidized to corresponding alcohols by potassium permanganate.



(13.24)

4. Isomerisation

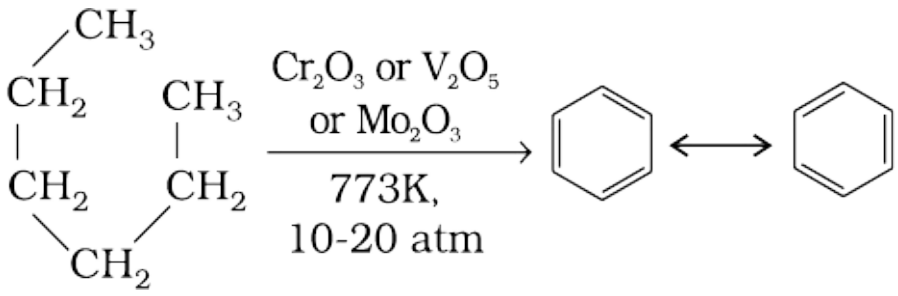
n-Alkanes on heating in the presence of anhydrous aluminium chloride and hydrogen chloride gas isomerise to branched chain alkanes. Major products are given below. Some minor products are also possible which you can think over. Minor products are generally not reported in organic reactions.



(13.25)

5. Aromatization

n-Alkanes having six or more carbon atoms on heating to 773K at 10-20 atmospheric pressure in the presence of oxides of vanadium, molybdenum or chromium supported over alumina get dehydrogenated and cyclised to benzene and its homologues. This reaction is known as aromatization or reforming.

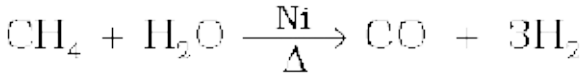


(13.26)

Toluene (C7H8) is methyl derivative of benzene. Which alkane do you suggest for preparation of toluene ?

6. Reaction with steam

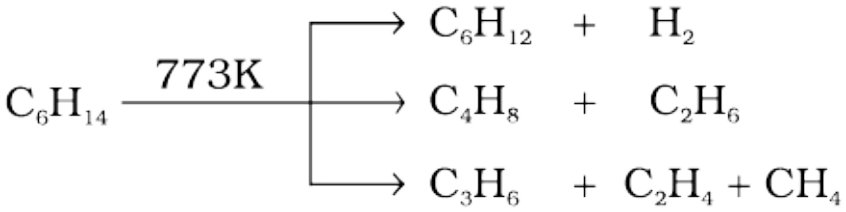
Methane reacts with steam at 1273 K in the presence of nickel catalyst to form carbon monoxide and dihydrogen. This method is used for industrial preparation of dihydrogen gas



(13.27)

7. Pyrolysis

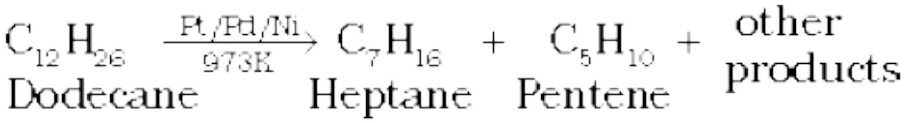
Higher alkanes on heating to higher temperature decompose into lower alkanes, alkenes etc. Such a decomposition reaction into smaller fragments by the application of heat is called pyrolysis or cracking.



(13.28)

Pyrolysis of alkanes is believed to be a free radical reaction. Preparation of oil gas or petrol gas from kerosene oil or petrol involves the principle of pyrolysis. For example, dodecane, a constituent of kerosene oil on

heating to 973K in the presence of platinum, palladium or nickel gives a mixture of heptane and pentene.



(13.29)

13.2.4 Conformations

Alkanes contain carbon-carbon sigma (σ) bonds. Electron distribution of the sigma molecular orbital is symmetrical around the internuclear axis of the C–C bond which is not disturbed due to rotation about its axis. This permits free rotation about C–C single bond. This rotation results into different spatial arrangements of atoms in space which can change into one another. Such spatial arrangements of atoms which can be converted into one another by rotation around a C-C single bond are called **conformations** or **conformers** or **rotamers**. Alkanes can thus have infinite number of conformations by rotation around C-C single bonds. However, it may be remembered that rotation around a C-C single bond is not completely free. It is hindered by a small energy barrier of 1-20 kJ mol–1 due to weak repulsive interaction between the adjacent bonds. Such a type of repulsive interaction is called **torsional strain**.

Conformations of ethane : Ethane molecule (C_2H_6) contains a carbon – carbon single bond with each carbon atom attached to three hydrogen atoms. Considering the ball and stick model of ethane, keep one carbon atom stationary and rotate the other carbon atom around the C-C axis. This rotation results into infinite number of spatial arrangements of hydrogen atoms attached to one carbon atom with respect to the hydrogen atoms attached to the other carbon atom. These are called **conformational isomers** (conformers). Thus there are infinite number of

conformations of ethane. However, there are two extreme cases. One such conformation in which hydrogen atoms attached to two carbons are as closed together as possible is called **eclipsed** conformation and the other in which hydrogens are as far apart as possible is known as the **staggered** conformation. Any other intermediate conformation is called a **skew** conformation.It may be remembered that in all the conformations, the bond angles and the bond lengths remain the same. Eclipsed and the staggered conformations can be represented by Sawhorse and Newman projections.

1. Sawhorse projections

In this projection, the molecule is viewed along the molecular axis. It is then projected on paper by drawing the central C–C bond as a somewhat longer straight line. Upper end of the line is slightly tilted towards right or left hand side. The front carbon is shown at the lower end of the line, whereas the rear carbon is shown at the upper end. Each carbon has three lines attached to it corresponding to three hydrogen atoms. The lines are inclined at an angle of 120° to each other. Sawhorse projections of eclipsed and staggered conformations of ethane are depicted in Fig. 13.2.

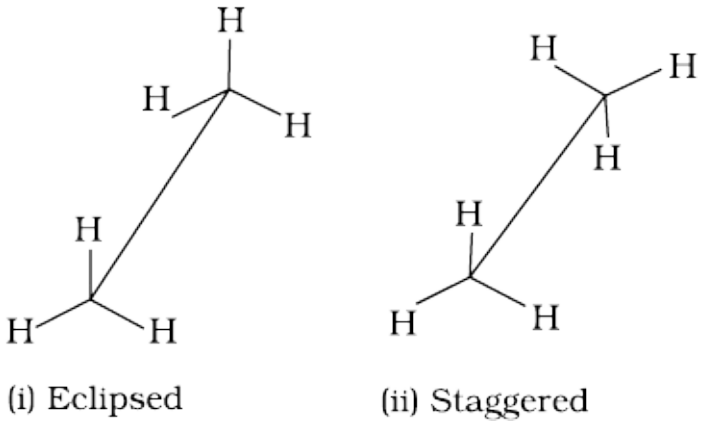


Fig. 13.2 Sawhorse projections of ethane

2. Newman projections

In this projection, the molecule is viewed at the C–C bond head on. The carbon atom nearer to the eye is represented by a point. Three hydrogen atoms attached to the front carbon atom are shown by three lines drawn at an angle of 120° to each other. The rear carbon atom (the carbon atom away from the eye) is represented by a circle and the three hydrogen atoms are shown attached to it by the shorter lines drawn at an angle of 120° to each other. The Newman's projections are depicted in Fig. 13.3.

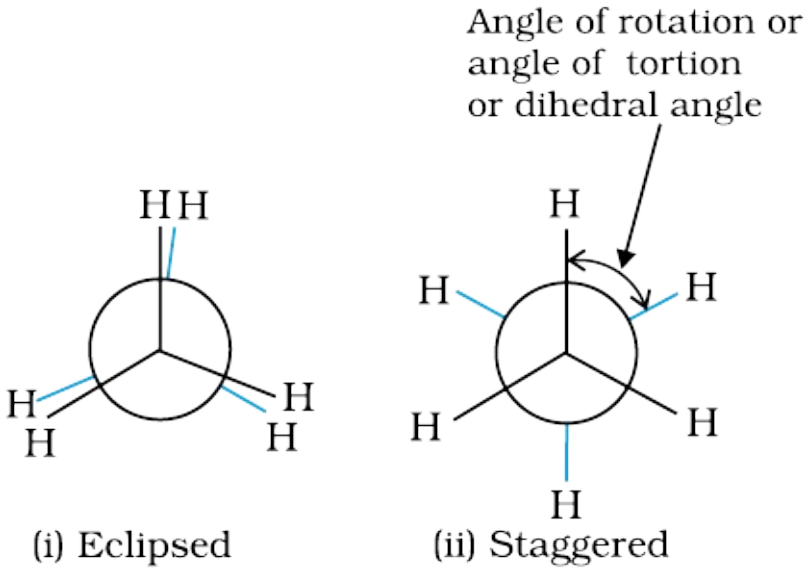


Fig. 13.3 Newman's projections of ethane

Relative stability of conformations: As mentioned earlier, in staggered form of ethane, the electron clouds of carbon-hydrogen bonds are as far apart as possible. Thus, there are minimum repulsive forces, minimum energy and maximum stability of the molecule. On the other hand, when the staggered form changes into the eclipsed form, the electron clouds of the carbon – hydrogen bonds come closer to each other resulting in increase in electron cloud repulsions. To check the increased repulsive

forces, molecule will have to possess more energy and thus has lesser stability. As already mentioned, the repulsive interaction between the electron clouds, which affects stability of a conformation, is called **torsional strain**. Magnitude of torsional strain depends upon the angle of rotation about C–C bond. This angle is also called **dihedral angle** or **torsional angle**. Of all the conformations of ethane, the staggered form has the least torsional strain and the eclipsed form, the maximum torsional strain. Therefore, staggered conformation is more stable than the eclipsed conformation. Hence, molecule largely remains in staggered conformation or we can say that it is preferred conformation. Thus it may be inferred that rotation around C–C bond in ethane is not completely free. The energy difference between the two extreme forms is of the order of 12.5 kJ mol–1, which is very small. Even at ordinary temperatures, the ethane molecule gains thermal or kinetic energy sufficient enough to overcome this energy barrier of 12.5 kJ mol–1 through intermolecular collisions. Thus, it can be said that rotation about carbon-carbon single bond in ethane is almost free for all practical purposes. It has not been possible to separate and isolate different conformational isomers of ethane.

13.3 ALKENES

Alkenes are unsaturated hydrocarbons containing at least one double bond. What should be the general formula of alkenes? If there is one double bond between two carbon atoms in alkenes, they must possess two hydrogen atoms less than alkanes. Hence, general formula for alkenes is C_nH_{2n}. Alkenes are also known as olefins (oil forming) since the first member, ethylene or ethene (C2H4) was found to form an oily liquid on reaction with chlorine.

13.3.1 Structure of Double Bond

Carbon-carbon double bond in alkenes consists of one strong sigma (σ) bond (bond enthalpy about 397 kJ mol–1) due to head-on overlapping of sp2 hybridised orbitals and one weak pi (π) bond (bond enthalpy about 284 kJ mol–1) obtained by lateral or sideways overlapping of the two 2p orbitals of the two carbon atoms. The double bond is shorter in bond length (134 pm) than the C–C single bond (154 pm). You have already read that the pi (π) bond is a weaker bond due to poor sideways overlapping between the two 2p orbitals. Thus, the presence of the pi (π) bond makes alkenes behave as sources of loosely held mobile electrons. Therefore, alkenes are easily attacked by reagents or compounds which are in search of electrons. Such reagents are called electrophilic reagents. The presence of weaker π-bond makes alkenes unstable molecules in comparison to alkanes and thus, alkenes can be changed into single bond compounds by combining with the electrophilic reagents. Strength of the double bond (bond enthalpy, 681 kJ mol–1) is greater than that of a carbon-carbon single bond in ethane (bond enthalpy, 348 kJ mol–1). Orbital diagrams of ethene molecule are shown in Figs. 13.4 and 13.5.

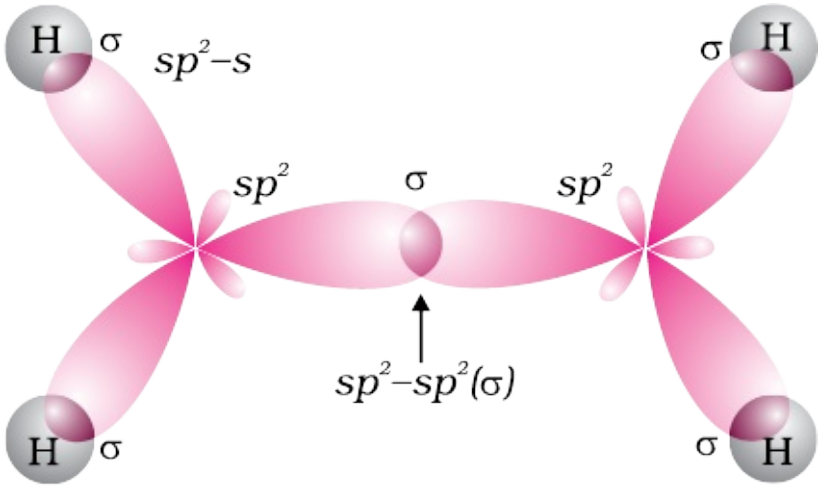


Fig. 13.4 Orbital picture of ethene depicting σ bonds only

13.3.2 Nomenclature

For nomenclature of alkenes in IUPAC system, the longest chain of carbon atoms containing the double bond is selected. Numbering of the chain is done from the end which is nearer to the double bond. The suffix 'ene' replaces 'ane' of alkanes. It may be remembered that first member of alkene series is: CH_2 (replacing n by 1 in C_nH_{2n}) known as methene but has a very short life. As already mentioned, first stable member of alkene series is C_2H_4 known as ethylene (common) or ethene (IUPAC). IUPAC names of a few members of alkenes are given below :

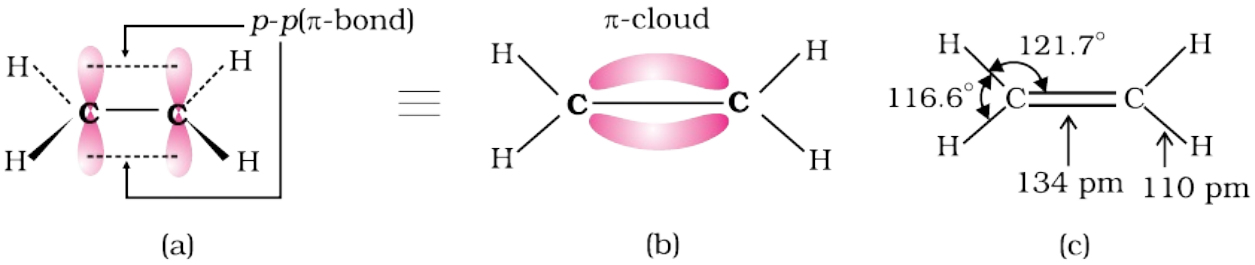


Fig. 13.5 Orbital picture of ethene showing formation of (a) π-bond, (b) π-cloud and (c) bond angles and bond lengths

Structure	IUPAC name
$CH_3 - CH = CH_2$	Propene
$CH_3 - CH_2 - CH = CH_2$	But – 1 - ene
$CH_3 - CH = CH - CH_3$	But-2-ene
$CH_2 = CH - CH = CH_2$	Buta – 1,3 - diene
$CH_2 = C(CH_3) - CH_3$	2-Methylprop-1-ene
$CH_2 = CH - CH(CH_3) - CH_3$	3-Methylbut-1-ene

Problem 13.7

Write IUPAC names of the following compounds:

(i) $(CH_3)_2CH - CH = CH - CH_2 - CH$

$CH_3 - CH - CH$

C_2H_5

(ii) 

(iii) $CH_2 = C(CH_2CH_2CH_3)_2$

(iv) $CH_3CH_2CH_2CH_2 \quad CH_2CH_3$

$CH_3 - CHCH = C - CH_2 - CHCH_3$

CH_3

Solution

(i) 2,8-Dimethyl-3, 6-decadiene;

(ii) 1,3,5,7 Octatetraene;

(iii) 2-n-Propylpent-1-ene;

(iv) 4-Ethyl-2,6-dimethyl-dec-4-ene;

Problem 13.8

Calculate number of sigma (σ) and pi (π) bonds in the above structures (i-iv).

Solution

σ bonds : 33, π bonds : 2

σ bonds : 17, π bonds : 4

σ bonds : 23, π bond : 1

σ bonds : 41, π bond : 1

13.3.3 Isomerism

Alkenes show both structural isomerism and geometrical isomerism.

Structural isomerism : As in alkanes, ethene (C_2H_4) and propene (C_3H_6) can have only one structure but alkenes higher than propene have different structures. Alkenes possessing C4H8 as molecular formula can be written in the following three ways:

I. $\overset{1}{CH_2} = \overset{2}{CH} - \overset{3}{CH_2} - \overset{4}{CH_3}$

But-1-ene

(C_4H_8)

II. $\overset{1}{CH_3} - \overset{2}{CH} = \overset{3}{CH} - \overset{4}{CH_3}$

But-2-ene

(C_4H_8)

III. $\overset{1}{CH_2} = \overset{2}{\underset{\displaystyle CH_3}{\underset{|}{C}}} - \overset{3}{CH_3}$

2-Methyprop-1-ene

(C_4H_8)

Structures I and III, and II and III are the examples of **chain isomerism** whereas structures I and II are **position isomers**.

Problem 13.9

Write structures and IUPAC names of different structural isomers of

alkenes corresponding to C_5H_{10}.

Solution

(a) $CH_2 = CH - CH_2 - CH_2 - CH_3$
Pent-1-ene

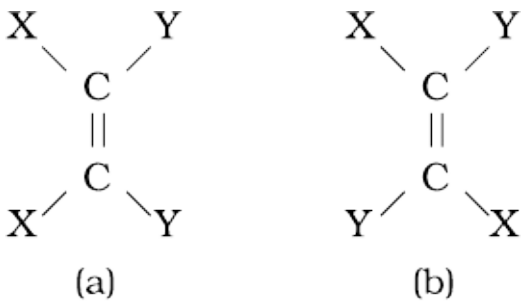
(b) $CH_3 - CH{=}CH - CH_2 - CH_3$
Pent-2-ene

(c) $CH_3 - C(CH_3) = CH - CH_3$
2-Methylbut-2-ene

(d) $CH_3 - CH(CH_3) - CH = CH_2$
3-Methylbut-1-ene

(e) $CH_2 = C(CH_3) - CH_2 - CH_3$
2-Methylbut-1-ene

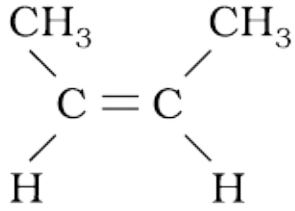
Geometrical isomerism: Doubly bonded carbon atoms have to satisfy the remaining two valences by joining with two atoms or groups. If the two atoms or groups attached to each carbon atom are different, they can be represented by YX C = C XY like structure. YX C = C XY can be represented in space in the following two ways :



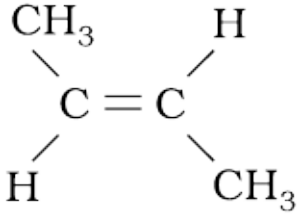
(a) (b)

In (a), the two identical atoms i.e., both the X or both the Y lie on the same side of the double bond but in (b) the two X or two Y lie across the

double bond or on the opposite sides of the double bond. This results in different geometry of (a) and (b) i.e. disposition of atoms or groups in space in the two arrangements is different. Therefore, they are stereoisomers. They would have the same geometry if atoms or groups around C=C bond can be rotated but rotation around C=C bond is not free. It is restricted. For understanding this concept, take two pieces of strong cardboards and join them with the help of two nails. Hold one cardboard in your one hand and try to rotate the other. Can you really rotate the other cardboard ? The answer is no. The rotation is restricted. This illustrates that the restricted rotation of atoms or groups around the doubly bonded carbon atoms gives rise to different geometries of such compounds. The stereoisomers of this type are called geometrical isomers. The isomer of the type (a), in which two identical atoms or groups lie on the same side of the double bond is called cis isomer and the other isomer of the type (b), in which identical atoms or groups lie on the opposite sides of the double bond is called trans isomer . Thus cis and trans isomers have the same structure but have different configuration (arrangement of atoms or groups in space). Due to different arrangement of atoms or groups in space, these isomers differ in their properties like melting point, boiling point, dipole moment, solubility etc. Geometrical or cis-trans isomers of but-2-ene are represented below :



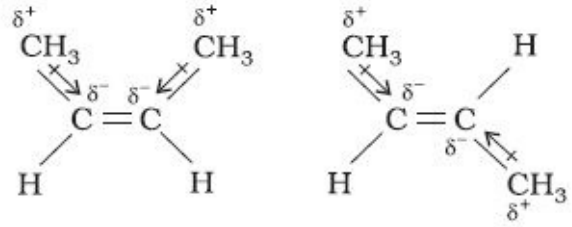
cis-But-2-ene
(b.p. 277 K)



trans-But-2-ene
(b.p. 274 K)

Cis form of alkene is found to be more polar than the trans form. For example, dipole moment of cis-but-2-ene is 0.33 Debye, whereas, dipole

moment of the trans form is almost zero or it can be said that trans-but-2-ene is non-polar. This can be understood by drawing geometries of the two forms as given below from which it is clear that in the trans-but-2-ene, the two methyl groups are in opposite directions, Threfore, dipole moments of C-CH3 bonds cancel, thus making the trans form non-polar.



cis-But-2-ene ($\mu = 0.33D$) *trans*-But-2-ene ($\mu = 0$)

In the case of solids, it is observed that the trans isomer has higher melting point than the cis form.

Geometrical or cis-trans isomerism is also shown by alkenes of the types XYC = CXZ and XYC = CZW

Problem 13.10

Draw cis and trans isomers of the following compounds. Also write their IUPAC names :

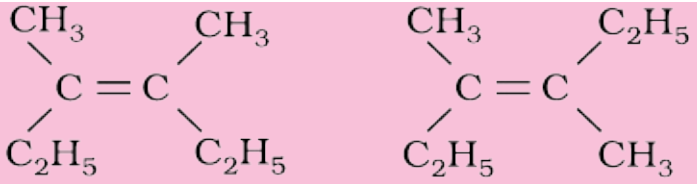
(i) CHCl = CHCl

(ii) $C_2H_5CCH_3 = CCH_3C_2H_5$

Solution



cis-1, 2-Dichloroethene *trans*-1, 2-Dichloroethene

(ii) 

cis-3, 4-Dimethylhex-3-ene *trans-3, 4-Dimethylhex -3-ene*

Problem 13.11

Which of the following compounds will show cis-trans isomerism?

(i) $(CH_3)_2C = CH - C_2H_5$

(ii) $CH_2 = CBr_2$

(iii) $C_6H_5CH = CH - CH_3$

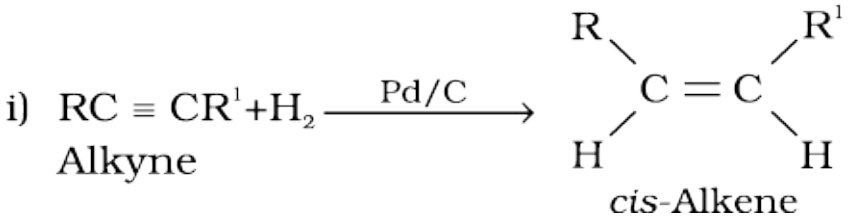
(iv) $CH_3CH = CCl\ CH_3$

Solution

(iii) and (iv). In structures (i) and (ii), two identical groups are attached to one of the doubly bonded carbon atom.

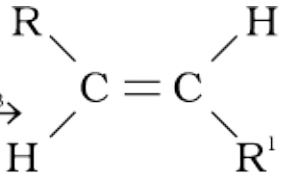
13.3.4 Preparation

1. From alkynes: Alkynes on partial reduction with calculated amount of dihydrogen in the presence of palladised charcoal partially deactivated with poisons like sulphur compounds or quinoline give alkenes. Partially deactivated palladised charcoal is known as Lindlar's catalyst. Alkenes thus obtained are having cis geometry. However, alkynes on reduction with sodium in liquid ammonia form trans alkenes.

i) 

cis-Alkene

(13.30)

ii) $RC \equiv CR^1 + H_2 \xrightarrow{Na/liquid\ NH_3}$ 

Alkyne *trans*-Alkene

(13.31)

iii) $CH \equiv CH + H_2 \xrightarrow{Pd/C} CH_2 = CH_2$ (13.32)

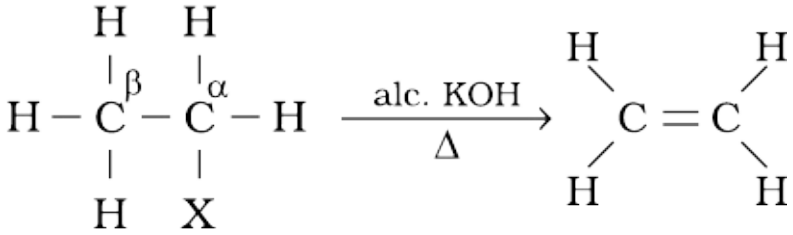
Ethyne Ethene

iv) $CH_3 - C \equiv CH + H_2 \xrightarrow{Pd/C} CH_3 - CH = CH_2$

Propyne Propene (13.33)

Will propene thus obtained show geometrical isomerism? Think for the reason in support of your answer.

2. From alkyl halides: Alkyl halides (R-X) on heating with alcoholic potash (potassium hydroxide dissolved in alcohol, say, ethanol) eliminate one molecule of halogen acid to form alkenes. This reaction is known as **dehydrohalogenation** i.e., removal of halogen acid. This is example of **β-elimination reaction**, since hydrogen atom is eliminated from the β carbon atom (carbon atom next to the carbon to which halogen is attached).



(X = Cl, Br, I)

(13.34)

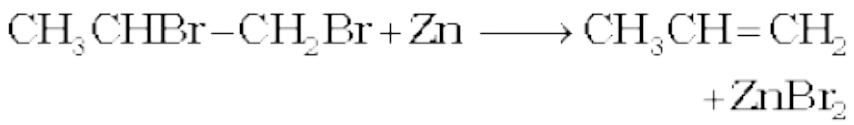
Nature of halogen atom and the alkyl group determine rate of the

reaction. It is observed that for halogens, the rate is: iodine > bromine > chlorine, while for alkyl groups it is : tert > secondary > primary.

3. From vicinal dihalides: Dihalides in which two halogen atoms are attached to two adjacent carbon atoms are known as vicinal dihalides. Vicinal dihalides on treatment with zinc metal lose a molecule of ZnX2 to form an alkene. This reaction is known as **dehalogenation**.

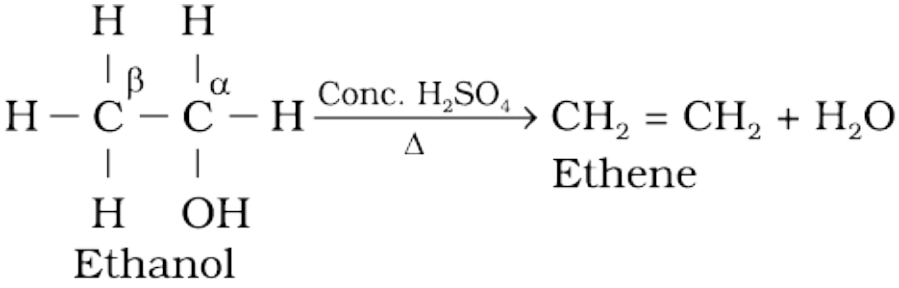


(13.35)



(13.36)

4. From alcohols by acidic dehydration: You have read during nomenclature of different homologous series in Unit 12 that alcohols are the hydroxy derivatives of alkanes. They are represented by R–OH where, R is C_nH_{2n+1}. Alcohols on heating with concentrated sulphuric acid form alkenes with the elimination of one water molecule. Since a water molecule is eliminated from the alcohol molecule in the presence of an acid, this reaction is known as **acidic dehydration of alcohols**. This reaction is also the example of β-elimination reaction since –OH group takes out one hydrogen atom from the β-carbon atom.



(13.37)

13.3.5 Properties

Physical properties

Alkenes as a class resemble alkanes in physical properties, except in types of isomerism and difference in polar nature. The first three members are gases, the next fourteen are liquids and the higher ones are solids. Ethene is a colourless gas with a faint sweet smell. All other alkenes are colourless and odourless, insoluble in water but fairly soluble in non-polar solvents like benzene, petroleum ether. They show a regular increase in boiling point with increase in size i.e., every – CH_2 group added increases boiling point by 20–30 K. Like alkanes, straight chain alkenes have higher boiling point than isomeric branched chain compounds.

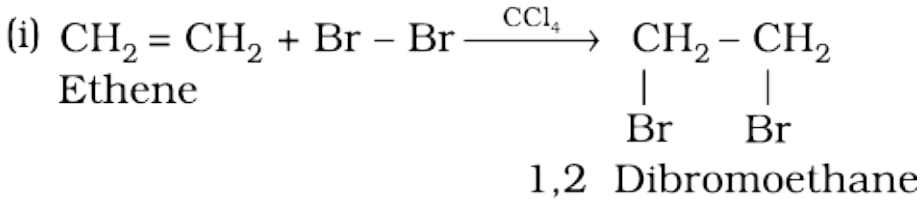
Chemical properties

Alkenes are the rich source of loosely held pi (π) electrons, due to which they show addition reactions in which the electrophiles add on to the carbon-carbon double bond to form the addition products. Some reagents also add by free radical mechanism. There are cases when under special conditions, alkenes also undergo free radical substitution reactions. Oxidation and ozonolysis reactions are also quite prominent in alkenes. A brief description of different reactions of alkenes is given below:

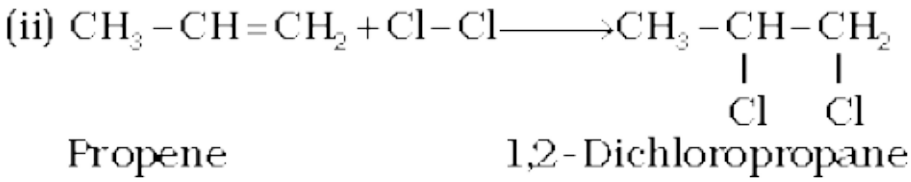
1. Addition of dihydrogen: Alkenes add up one molecule of dihydrogen gas in the presence of finely divided nickel, palladium or platinum to form alkanes (Section 13.2.2)

2. Addition of halogens : Halogens like bromine or chlorine add up to alkene to form vicinal dihalides. However, iodine does not show addition reaction under normal conditions. The reddish orange colour of bromine

solution in carbon tetrachloride is discharged when bromine adds up to an unsaturation site. This reaction is used as a test for unsaturation. Addition of halogens to alkenes is an example of electrophilic addition reaction involving cyclic halonium ion formation which you will study in higher classes.



(13.38)



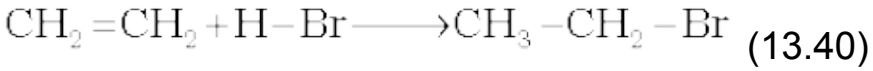
(13.39)

3. Addition of hydrogen halides: Hydrogen halides (HCl, HBr,HI) add up to alkenes to form alkyl halides. The order of reactivity of the hydrogen halides is

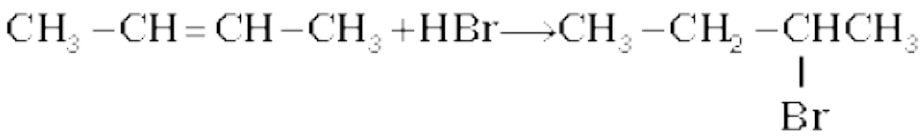
HI > HBr > HCl. Like addition of halogens to alkenes, addition of hydrogen halides is also an example of electrophilic addition reaction. Let us illustrate this by taking addition of HBr to symmetrical and unsymmetrical alkenes

Addition reaction of HBr to symmetrical alkenes

Addition reactions of HBr to symmetrical alkenes (similar groups attached to double bond) take place by electrophilic addition mechanism.



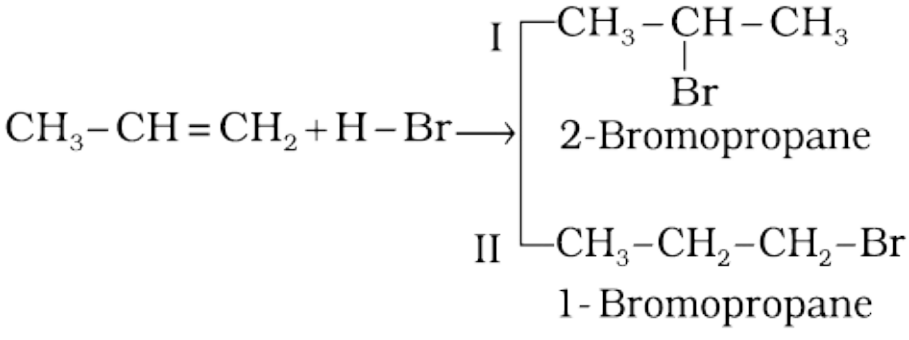
(13.40)



(13.41)

Addition reaction of HBr to unsymmetrical alkenes (Markovnikov Rule)

How will H – Br add to propene ? The two possible products are I and II.

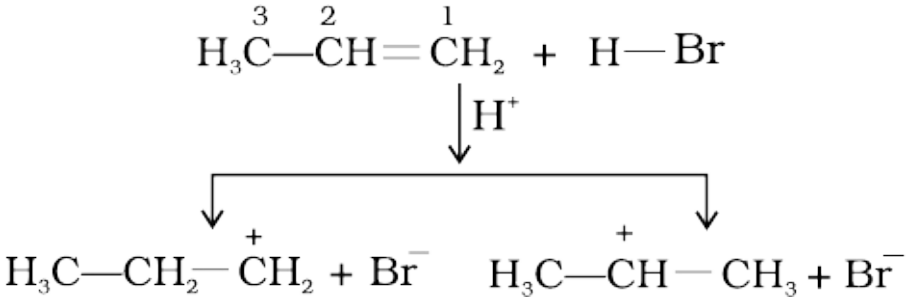


(13.42)

Markovnikov, a Russian chemist made a generalisation in 1869 after studying such reactions in detail. These generalisations led Markovnikov to frame a rule called Markovnikov rule. The rule states that negative part of the addendum (adding molecule) gets attached to that carbon atom which possesses lesser number of hydrogen atoms. Thus according to this rule, product I i.e., 2-bromopropane is expected. In actual practice, this is the principal product of the reaction. This generalisation of Markovnikov rule can be better understood in terms of mechanism of the reaction.

Mechanism

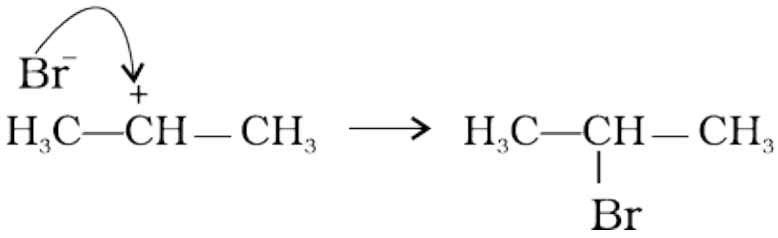
Hydrogen bromide provides an electrophile, H+, which attacks the double bond to form carbocation as shown below :



(a) less stable primary carbocation (b) more stable secondary carbocation

(i) The secondary carbocation (b) is more stable than the primary carbocation (a), therefore, the former predominates because it is formed at a faster rate.

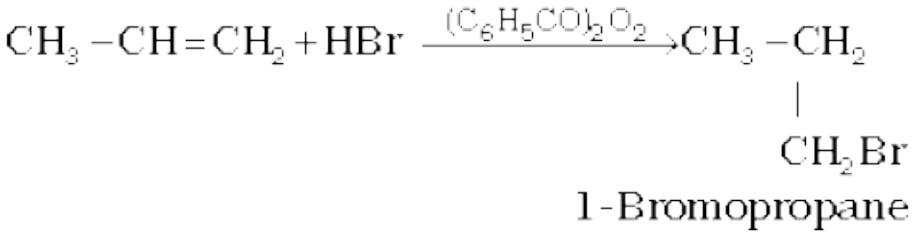
(ii) The carbocation (b) is attacked by Br– ion to form the product as follows :



2-Bromopropane (major product)

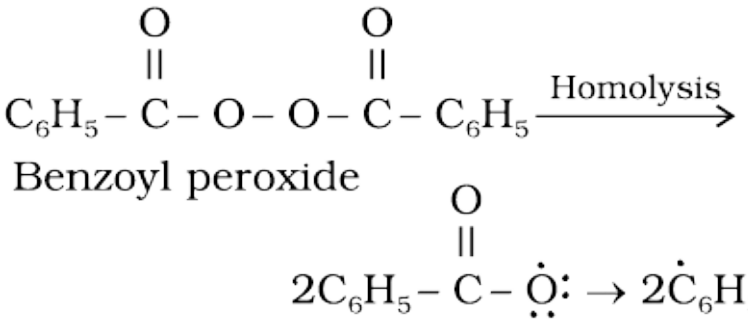
Anti Markovnikov addition or peroxide effect or Kharash effect

In the presence of peroxide, addition of HBr to unsymmetrical alkenes like propene takes place contrary to the Markovnikov rule. This happens only with HBr but not with HCl and HI. This addition reaction was observed by M.S. Kharash and F.R. Mayo in 1933 at the University of Chicago. This reaction is known as peroxide or Kharash effect or addition reaction anti to Markovnikov rule.

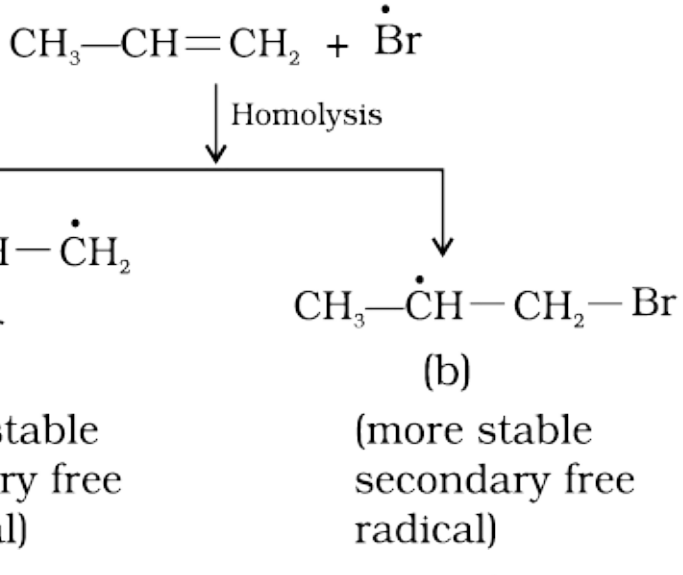


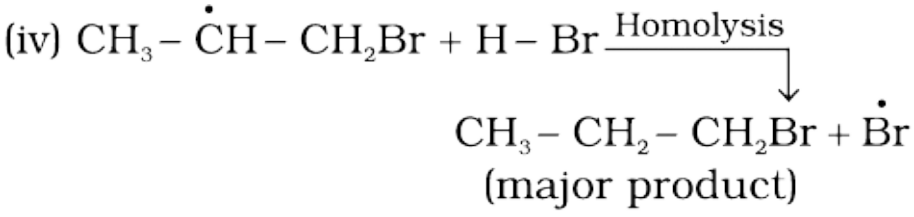
(13.43)

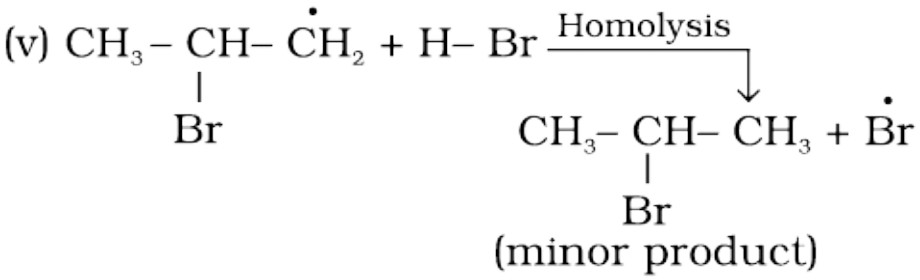
Mechanism : Peroxide effect proceeds via free radical chain mechanism as given below:



(ii) 

(iii) 

(iv) 



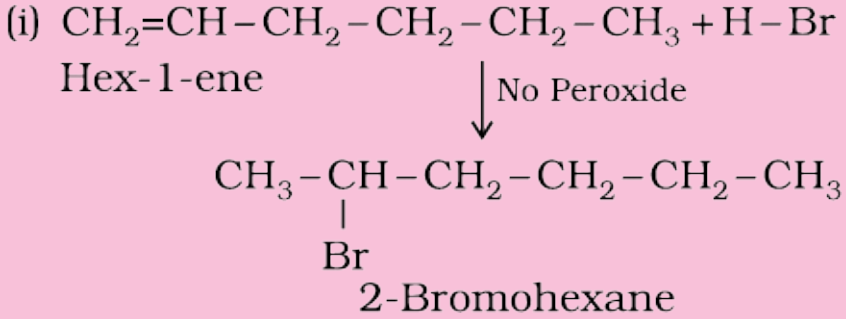
The secondary free radical obtained in the above mechanism (step iii) is more stable than the primary. This explains the formation of 1-bromopropane as the major product. It may be noted that the peroxide effect is not observed in addition of HCl and HI. This may be due to the fact that the H–Cl bond being stronger (430.5 kJ mol–1) than H–Br bond (363.7 kJ mol–1), is not cleaved by the free radical, whereas the H–I bond is weaker (296.8 kJ mol–1) and iodine free radicals combine to form iodine molecules instead of adding to the double bond.

Problem 13.12

Write IUPAC names of the products obtained by addition reactions of HBr to hex-1-ene

(i) in the absence of peroxide and
(ii) in the presence of peroxide.

Solution



(ii) $CH_2=CH-CH_2-CH_2-CH_2-CH_3 + H-Br$

$\xrightarrow{\text{Peroxide}}$

$CH_2-CH_2-CH_2-CH_2-CH_2-CH_3$

$|$

Br

1-Bromohexane

4. Addition of sulphuric acid : Cold concentrated sulphuric acid adds to alkenes in accordance with Markovnikov rule to form alkyl hydrogen sulphate by the electrophilic addition reaction.

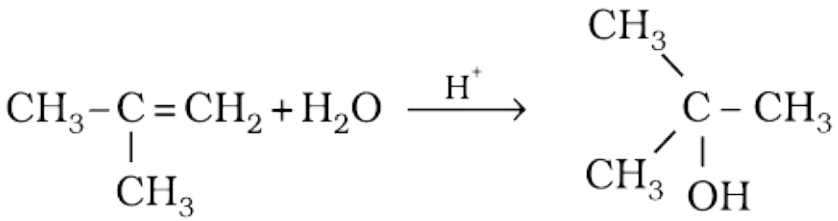
$$CH_2 = CH_2 + H - O - \underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}} - O - H \longrightarrow CH_3 - CH_2 - O\,SO_2 - OH \text{ or } C_2H_5HSO_4$$

Ethyl hydrogen sulphate (13.44)

$$CH_3 - CH = CH_2 + HOSO_2OH \longrightarrow CH_3 - \underset{\underset{OSO_2OH}{|}}{CH} - CH_3$$

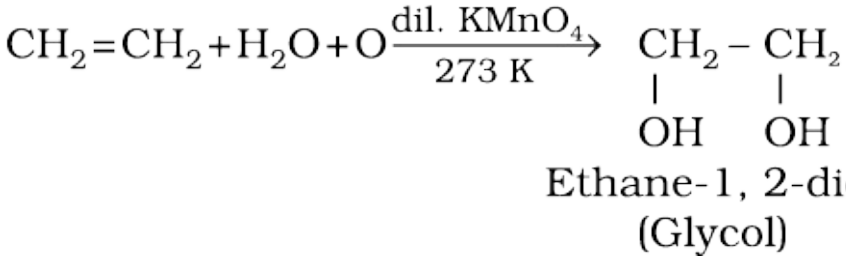
Propyl hydrogen sulphate (13.45)

5. Addition of water : In the presence of a few drops of concentrated sulphuric acid alkenes react with water to form alcohols, in accordance with the Markovnikov rule.

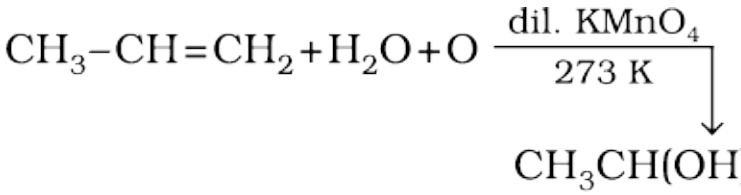


2-Methylpropene 2-Methylpropan-2-ol (13.46)

6. Oxidation: Alkenes on reaction with cold, dilute, aqueous solution of potassium permanganate (Baeyer's reagent) produce vicinal glycols. Decolorisation of KMnO4 solution is used as a test for unsaturation.

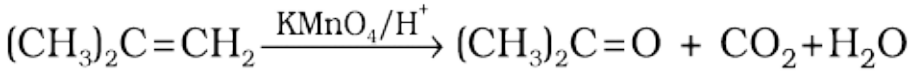


Ethane-1, 2-diol
(Glycol) (13.47)

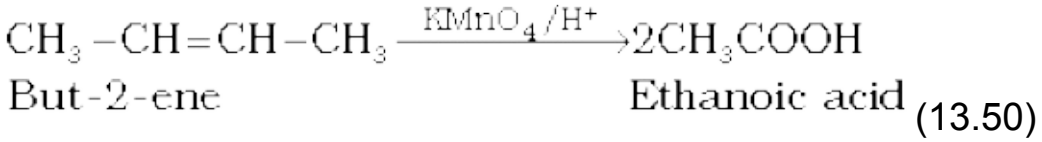


Propane-1, 2-diol (13.48)

b) Acidic potassium permanganate or acidic potassium dichromate oxidises alkenes to ketones and/or acids depending upon the nature of the alkene and the experimental conditions

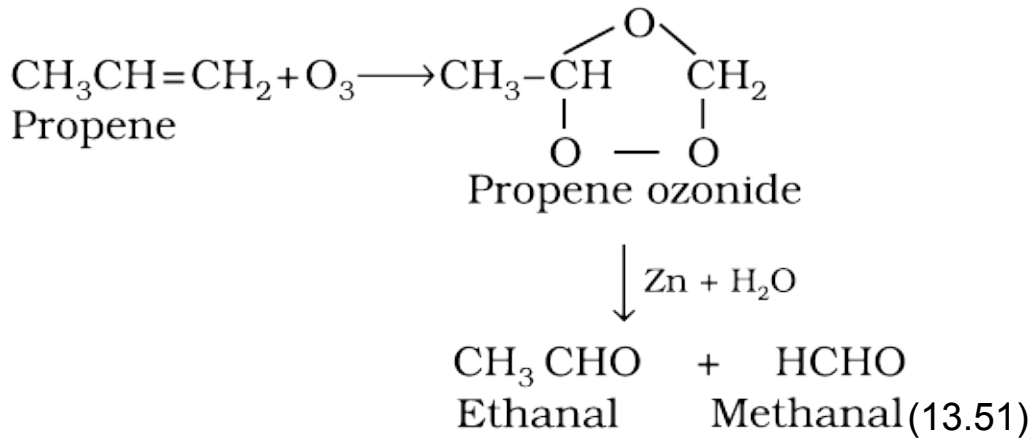


2-Methlypropene Propan-2-one (13.49)

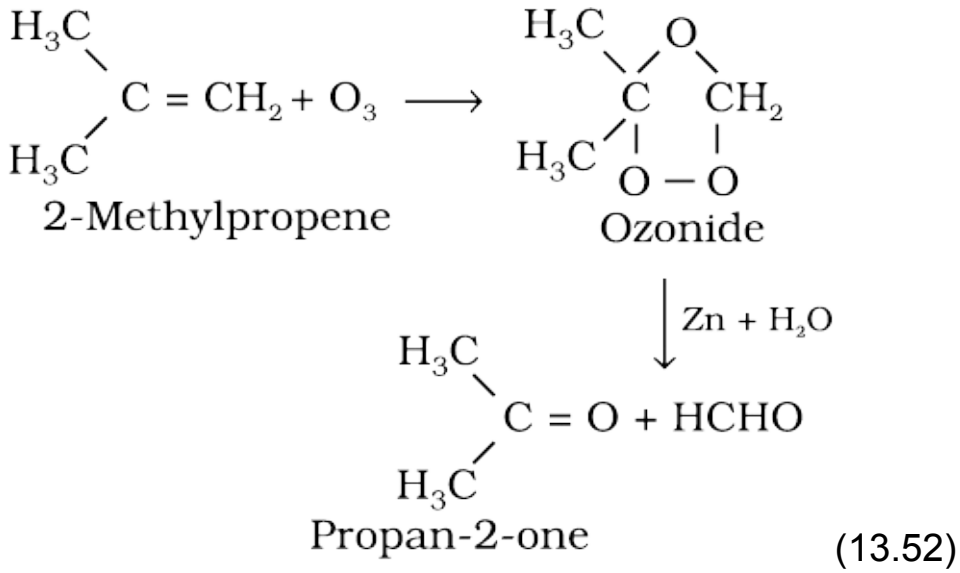


(13.50)

7. Ozonolysis : Ozonolysis of alkenes involves the addition of ozone molecule to alkene to form ozonide, and then cleavage of the ozonide by Zn-H2O to smaller molecules. This reaction is highly useful in detecting the position of the double bond in alkenes or other unsaturated compounds.

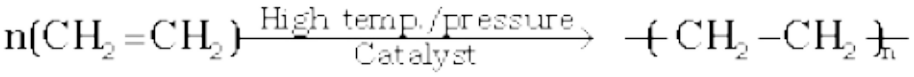


(13.51)



(13.52)

8. Polymerisation: You are familiar with polythene bags and polythene sheets. Polythene is obtained by the combination of large number of ethene molecules at high temperature, high pressure and in the presence of a catalyst. The large molecules thus obtained are called polymers. This reaction is known as polymerisation. The simple compounds from which polymers are made are called monomers. Other alkenes also undergo polymerisation.



(13.53)



(13.54)

Polymers are used for the manufacture of plastic bags, squeeze bottles, refrigerator dishes, toys, pipes, radio and T.V. cabinets etc. Polypropene is used for the manufacture of milk crates, plastic buckets and other moulded articles. Though these materials have now become common, excessive use of polythene and polypropylene is a matter of great concern for all of us.

13.4 ALKYNES

Like alkenes, alkynes are also unsaturated hydrocarbons. They contain at least one triple bond between two carbon atoms. The number of hydrogen atoms is still less in alkynes as compared to alkenes or alkanes. Their general formula is C_nH_{2n-2}.

The first stable member of alkyne series is ethyne which is popularly known as acetylene. Acetylene is used for arc welding purposes in the form of oxyacetylene flame obtained by mixing acetylene with oxygen gas. Alkynes are starting materials for a large number of organic compounds. Hence, it is interesting to study this class of organic compounds.

13.4.1 Nomenclature and Isomerism

In common system, alkynes are named as derivatives of acetylene. In IUPAC system, they are named as derivatives of the corresponding alkanes replacing 'ane' by the suffix 'yne'. The position of the triple bond is indicated by the first triply bonded carbon. Common and IUPAC names of a few members of alkyne series are given in Table 13.2.

You have already learnt that ethyne and propyne have got only one structure but there are two possible structures for butyne – (i) but-1-yne and (ii) but-2-yne. Since these two compounds differ in their structures due to the position of the triple bond, they are known as position isomers. In how many ways, you can construct the structure for the next homologue i.e., the next alkyne with molecular formula C5H8? Let us try to arrange five carbon atoms with a continuous chain and with a side chain. Following are the possible structures :

	Structure	IUPAC name
I.	$HC^{1}\equiv C^{2}-CH_2^{3}-CH_2^{4}-CH_3^{5}$	Pent–1-yne
II.	$H_3C^{1}-C^{2}\equiv C^{3}-CH_2^{4}-CH_3^{5}$	Pent–2-yne
III.	$H_3C^{4}-CH^{3}(CH_3)-C^{2}\equiv CH^{1}$	3-Methylbut–1-yne

Structures I and II are position isomers and structures I and III or II and III

are chain isomers.

Table 13.2 Common and IUPAC Names of Alkynes (C_nH_{2n-2})

Value of n	Formula	Structure	Common name	IUPAC name
2	C_2H_2	H-C≡CH	Acetylene	Ethyne
3	C_3H_4	CH_3-C≡CH	Methylacetylene	Propyne
4	C_4H_6	CH_3CH_2-C≡CH	Ethylacetylene	But-1-yne
4	C_4H_6	CH_3-C≡C-CH_3	Dimethylacetylene	But-2-yne

Problem 13.13

Write structures of different isomers corresponding to the 5th member of alkyne series. Also write IUPAC names of all the isomers. What type of isomerism is exhibited by different pairs of isomers?

Solution

5th member of alkyne has the molecular formula C_6H_{10}. The possible isomers are:

(a) $HC \equiv C - CH_2 - CH_2 - CH_2 - CH_3$

Hex-1-yne

(b) $CH_3 - C \equiv C - CH_2 - CH_2 - CH_3$

Hex-2-yne

Value of n Formula Structure Common name IUPAC name

2 C_2H_2 H-C≡CH Acetylene Ethyne

3 C_3H_4 CH_3-C≡CH Methylacetylene Propyne

4 C_4H_6 CH_3CH_2-C≡CH Ethylacetylene But-1-yne

4 C_4H_6 CH_3-C≡C-CH_3 Dimethylacetylene But-2-yne

(c) $CH_3 – CH_2 – C \equiv C – CH_2 – CH_3$

Hex-3-yne

(d) $HC \equiv C – \underset{\displaystyle CH_3}{\underset{|}{CH}} – CH_2 – CH_3$

3-Methylpent-1-yne

(e) $HC \equiv C – CH_2 – \underset{\displaystyle CH_3}{\underset{|}{CH}} – CH_3$

(f) $CH_3 – C \equiv C – \underset{\displaystyle CH_3}{\underset{|}{CH}} – CH_3$

4-Methylpent-1-yne

4-Methylpent-2-yne

(g) $HC \equiv C – \underset{\displaystyle CH_3}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{C}}}} – CH_3$

3,3-Dimethylbut-1-yne

Position and chain isomerism shown by different pairs.

13.4.2 Structure of Triple Bond

Ethyne is the simplest molecule of alkyne series. Structure of ethyne is shown in Fig. 13.6.

Each carbon atom of ethyne has two sp hybridised orbitals. Carbon-carbon sigma (σ) bond is obtained by the head-on overlapping of the two sp hybridised orbitals of the two carbon atoms. The remaining sp hybridised orbital of each carbon atom undergoes overlapping along the

internuclear axis with the 1s orbital of each of the two hydrogen atoms forming two C-H sigma bonds. H-C-C bond angle is of 180°. Each carbon has two unhybridised p orbitals which are perpendicular to each other as well as to the plane of the C-C sigma bond. The 2p orbitals of one carbon atom are parallel to the 2p orbitals of the other carbon atom, which undergo lateral or sideways overlapping to form two pi (π) bonds between two carbon atoms. Thus ethyne molecule consists of one C–C σ bond, two C–H σ bonds and two C–C π bonds. The strength of C≡C bond (bond enthalpy 823 kJ mol-1) is more than those of C=C bond (bond enthalpy 681 kJ mol–1) and C–C bond (bond enthalpy 348 kJ mol–1). The C≡C bond length is shorter (120 pm) than those of C=C (133 pm) and C–C (154 pm). Electron cloud between two carbon atoms is cylindrically symmetrical about the internuclear axis. Thus, ethyne is a linear molecule.

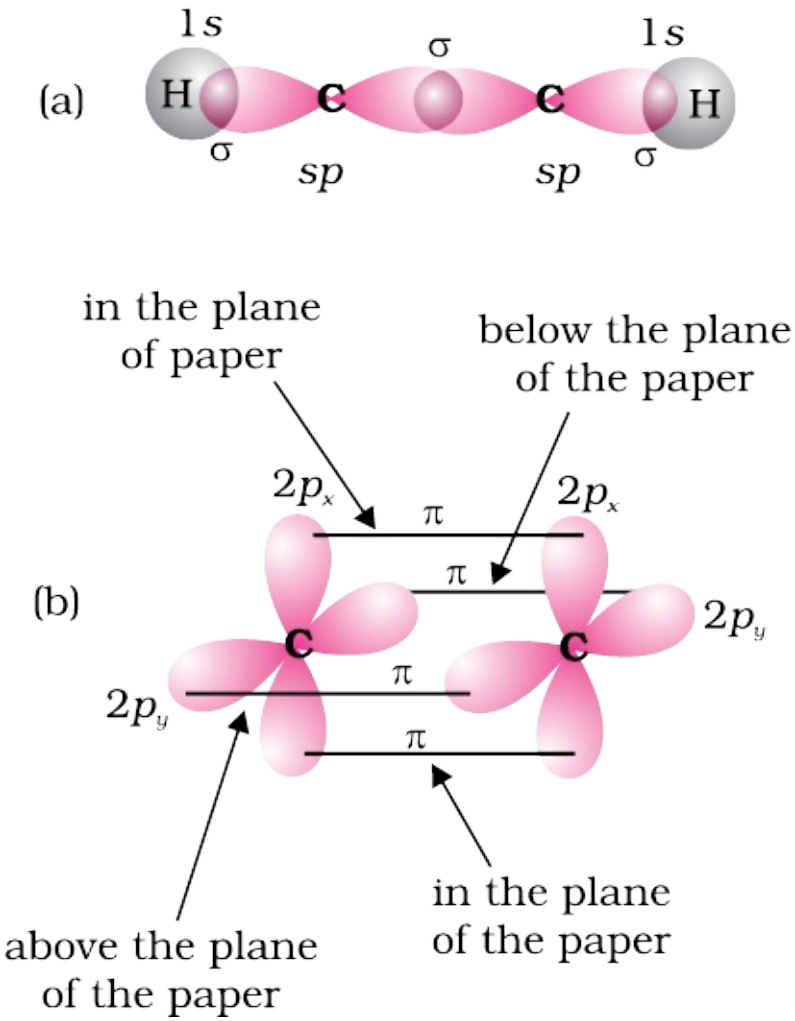


Fig. 13.6 Orbital picture of ethyne showing

(a) sigma overlaps (b) pi overlaps.

13.4.3 Preparation

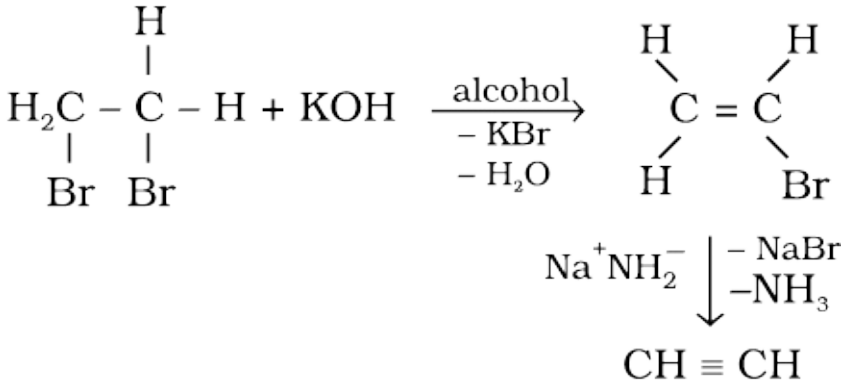
1. From calcium carbide: On industrial scale, ethyne is prepared by treating calcium carbide with water. Calcium carbide is prepared by heating quick lime with coke. Quick lime can be obtained by heating limestone as shown in the following
reactions:

$$CaCO_3 \xrightarrow{\Delta} CaO + CO_2 \quad (13.55)$$

$$CaO + 3C \longrightarrow \underset{\text{Calcium carbide}}{CaC_2} + CO \quad (13.56)$$

$$CaC_2 + 2H_2O \longrightarrow Ca(OH)_2 + C_2H_2 \quad (13.57)$$

2. From vicinal dihalides : Vicinal dihalides on treatment with alcoholic potassium hydroxide undergo dehydrohalogenation. One molecule of hydrogen halide is eliminated to form alkenyl halide which on treatment with sodamide gives alkyne.



13.4.4 Properties

Physical properties

Physical properties of alkynes follow the same trend of alkenes and alkanes. First three members are gases, the next eight are liquids and the higher ones are solids. All alkynes are colourless. Ethyene has characteristic odour. Other members are odourless. Alkynes are weakly polar in nature. They are lighter than water and immiscible with water but soluble in organic solvents like ethers, carbon tetrachloride and benzene. Their melting point, boiling point and density increase with increase in molar mass.

Chemical properties

Alkynes show acidic nature, addition reactions and polymerisation reactions as follows :

A. Acidic character of alkyne: Sodium metal and sodamide ($NaNH_2$) are strong bases. They react with ethyne to form sodium acetylide with the liberation of dihydrogen gas. These reactions have not been observed in case of ethene and ethane thus indicating that ethyne is acidic in nature in comparison to ethene and ethane. Why is it so ? Has it something to do with their structures and the hybridisation ? You have read that hydrogen atoms in ethyne are attached to the sp hybridised carbon atoms whereas they are attached to sp2 hybridised carbon atoms in ethene and sp3 hybridised carbons in ethane. Due to the maximum percentage of s character (50%), the sp hybridised orbitals of carbon atoms in ethyne molecules have highest electronegativity; hence, these attract the shared electron pair of the C-H bond of ethyne to a greater extent than that of the sp2 hybridised orbitals of carbon in ethene and the sp3 hybridised orbital of carbon in ethane. Thus in ethyne, hydrogen atoms can be liberated as protons more easily as compared to ethene and ethane. Hence, hydrogen atoms of ethyne attached to triply bonded carbon atom are acidic in nature. You may note that the hydrogen atoms attached to the triply bonded carbons are acidic but not all the hydrogen atoms of alkynes.

$$HC \equiv CH + Na \rightarrow \underset{\text{Monosodium ethynide}}{HC \equiv C^{-}Na^{+}} + \tfrac{1}{2}H_2 \qquad (13.59)$$

$$HC \equiv C^-Na^+ + Na \rightarrow Na^+C^- \equiv C^-Na^+ + \tfrac{1}{2}H_2$$

Disodium ethynide (13.60)

$$CH_3 - C \equiv C - H \quad + \quad Na^+NH_2^-$$

$$\downarrow$$

$$CH_3 - C \equiv C^-Na^+ \quad + \quad NH_3$$

Sodium propynide (13.61)

These reactions are not shown by alkenes and alkanes, hence used for distinction between alkynes, alkenes and alkanes. What about the above reactions with but-1-yne and but-2-yne ? Alkanes, alkenes and alkynes follow the following trend in their acidic behaviour :

i) $HC \equiv CH > H_2C = CH_2 > CH_3 - CH_3$

ii) $HC \equiv CH > CH_3 - C \equiv CH >> CH_3 - C \equiv C - CH_3$

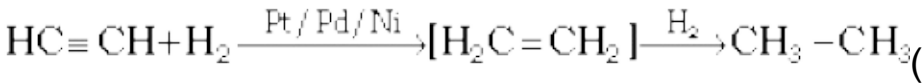
B. Addition reactions: Alkynes contain a triple bond, so they add up, two molecules of dihydrogen, halogen, hydrogen halides etc. Formation of the addition product takes place according to the following steps.

$$-C \equiv C- + H-Z \xrightarrow{H^+} -\overset{H}{\underset{|}{C}}=\overset{\oplus}{C}- + :\bar{Z} \longrightarrow -\overset{H}{\underset{|}{C}}=\overset{Z}{\underset{|}{C}}-$$

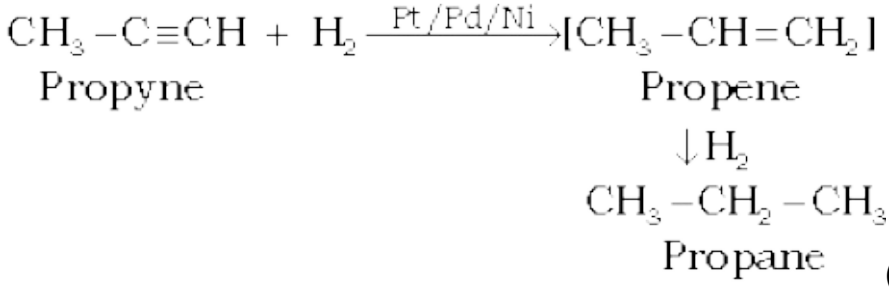
Vinylic cation

The addition product formed depends upon stability of vinylic cation. Addition in unsymmetrical alkynes takes place according to Markovnikov rule. Majority of the reactions of alkynes are the examples of electrophilic addition reactions. A few addition reactions are given below:

(i) Addition of dihydrogen

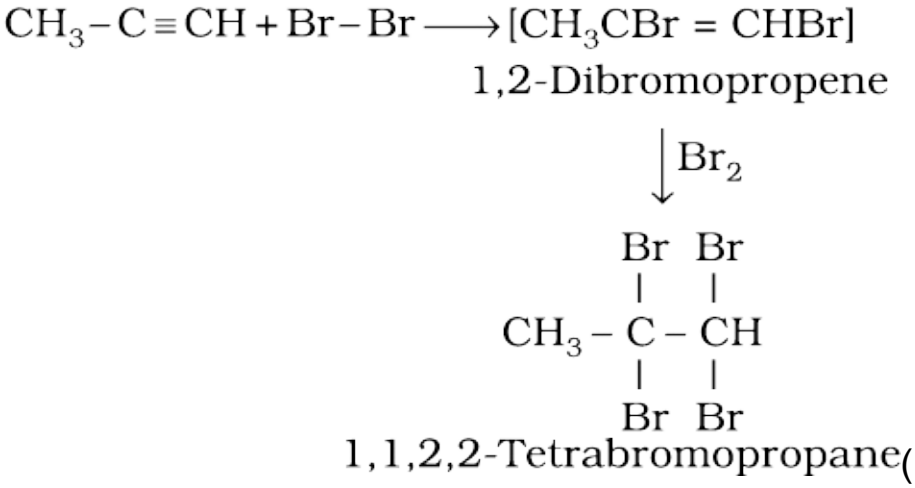


(13.62)



(13.63)

(ii) Addition of halogens

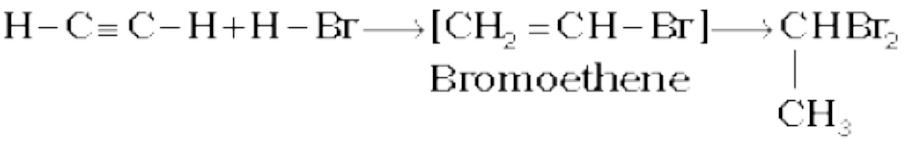


(13.64)

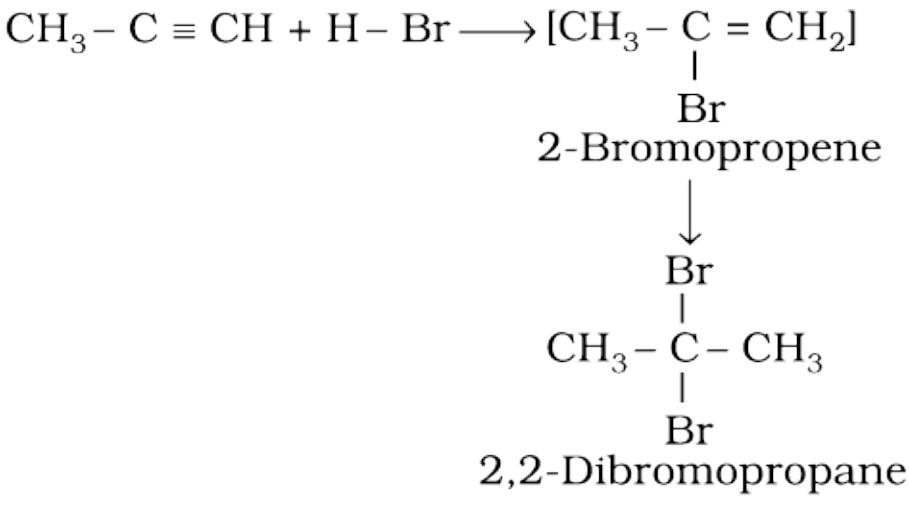
Reddish orange colour of the solution of bromine in carbon tetrachloride is decolourised. This is used as a test for unsaturation.

(iii) Addition of hydrogen halides

Two molecules of hydrogen halides (HCl, HBr, HI) add to alkynes to form gem dihalides (in which two halogens are attached to the same carbon atom)



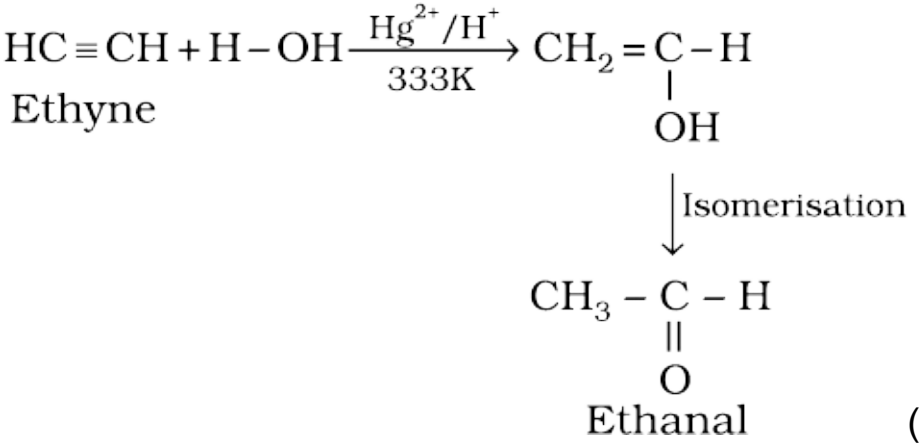
(13.65)



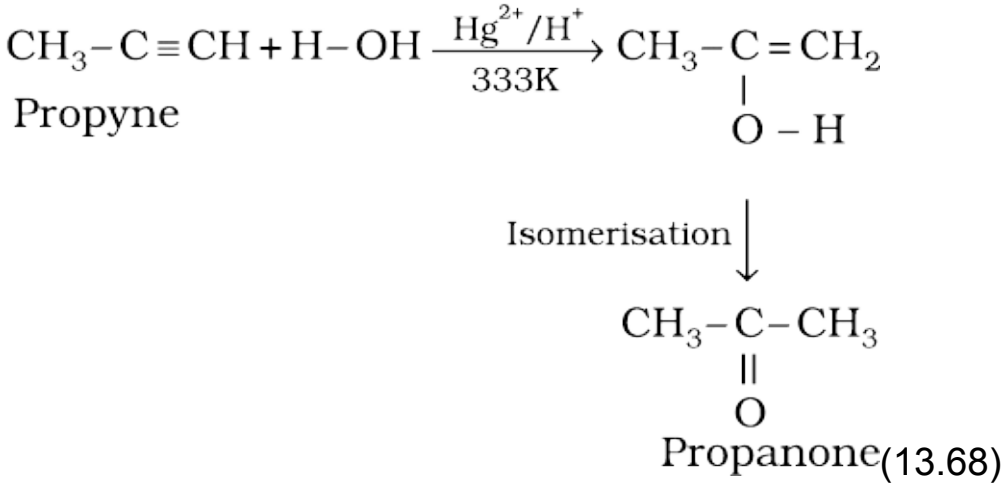
(13.66)

(iv) Addition of water

Like alkanes and alkenes, alkynes are also immiscible and do not react with water. However, one molecule of water adds to alkynes on warming with mercuric sulphate and dilute sulphuric acid at 333 K to form carbonyl compounds.



(13.67)



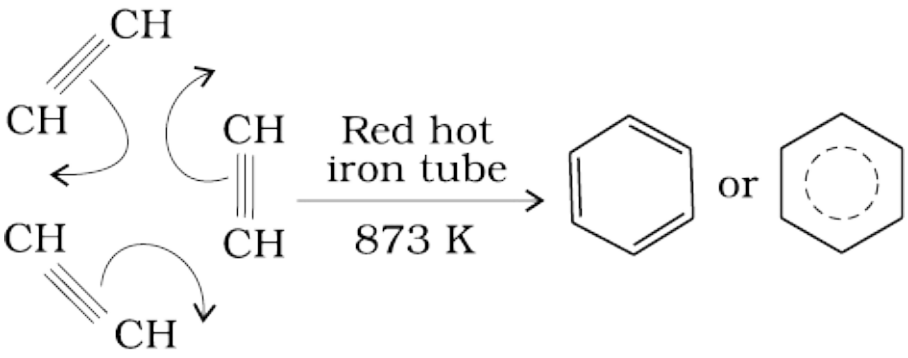
(13.68)

(v) Polymerisation

(a) Linear polymerisation: Under suitable conditions, linear polymerisation of ethyne takes place to produce polyacetylene or polyethyne which is a high molecular weight polyene containing repeating units of

(CH = CH – CH = CH) and can be represented as —(CH = CH – CH = CH)n— Under special conditions, this polymer conducts electricity. Thin film of polyacetylene can be used as electrodes in batteries. These films are good conductors, lighter and cheaper than the metal conductors.

(b) Cyclic polymerisation: Ethyne on passing through red hot iron tube at 873K undergoes cyclic polymerization. Three molecules polymerise to form benzene, which is the starting molecule for the preparation of derivatives of benzene, dyes, drugs and large number of other organic compounds. This is the best route for entering from aliphatic to aromatic compounds as discussed below:

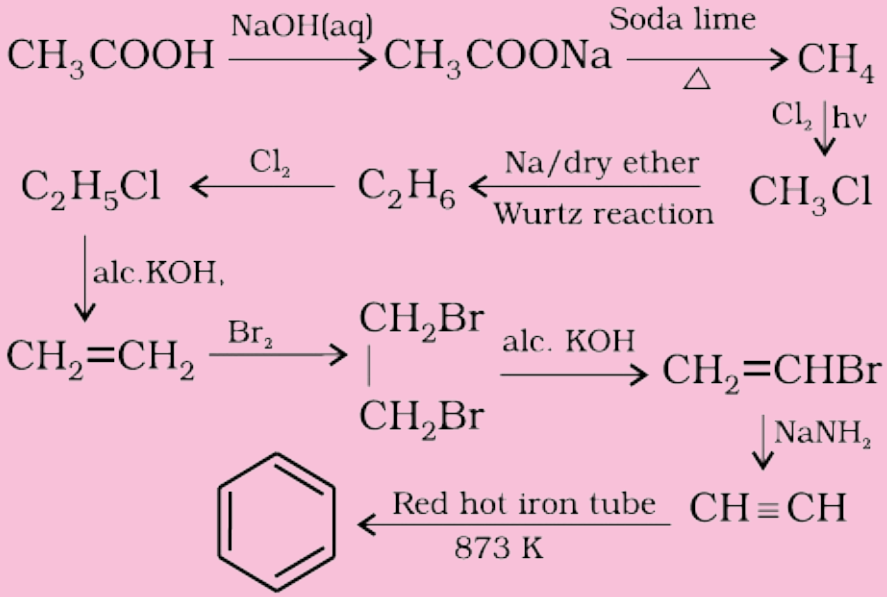


(13.69)

Problem 13.14

How will you convert ethanoic acid into benzene?

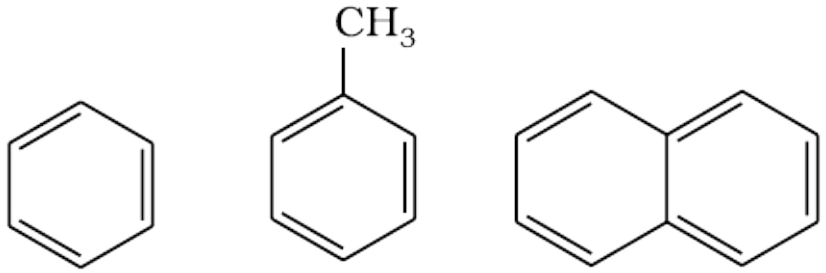
Solution



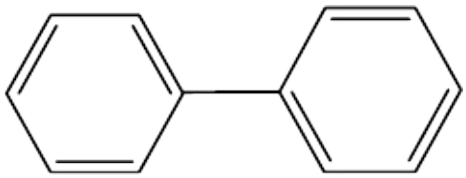
13.5 AROMATIC HYDROCARBON

These hydrocarbons are also known as ‘arenes’. Since most of them possess pleasant odour (Greek; aroma meaning pleasant smelling), the class of compounds was named as ‘aromatic compounds’. Most of such

compounds were found to contain benzene ring. Benzene ring is highly unsaturated but in a majority of reactions of aromatic compounds, the unsaturation of benzene ring is retained. However, there are examples of aromatic hydrocarbons which do not contain a benzene ring but instead contain other highly unsaturated ring. Aromatic compounds containing benzene ring are known as benzenoids and those not containing a benzene ring are known as non-benzenoids. Some examples of arenes are given
below:



Benzene Toluene Naphthalene

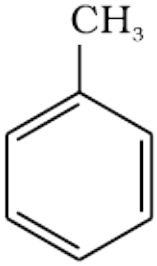


Biphenyl

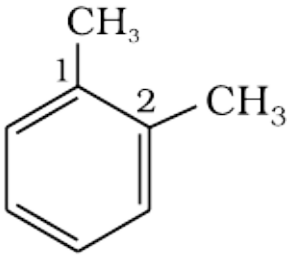
13.5.1 Nomenclature and Isomerism

The nomenclature and isomerism of aromatic hydrocarbons has already been discussed in Unit 12. All six hydrogen atoms in benzene are equivalent; so it forms one and only one type of monosubstituted product. When two hydrogen atoms in benzene are replaced by two similar or different monovalent atoms or groups, three different position isomers are possible. The 1, 2 or 1, 6 is known as the ortho (o–), the 1, 3 or 1, 5 as meta (m–) and the 1, 4 as para (p–) disubstituted compounds. A few

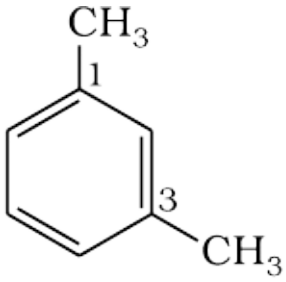
examples of derivatives of benzene are given below:



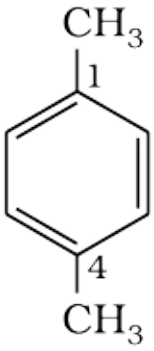
Methylbenzene(Toluene)



1,2-Dimethylbenzene (o-Xylene)



1,3 Dimethylbenzene (m-Xylene)



1,4-Dimethylbenzene (p-Xylene)

13.5.2 Structure of Benzene

Benzene was isolated by Michael Faraday in 1825. The molecular formula of benzene, C6H6, indicates a high degree of unsaturation. This molecular formula did not account for its relationship to corresponding alkanes, alkenes and alkynes which you have studied in earlier sections of this unit. What do you think about its possible structure? Due to its unique properties and unusual stability, it took several years to assign its structure. Benzene was found to be a stable molecule and found to form a triozonide which indicates the presence of three double bonds. Benzene was further found to produce one and only one monosubstituted

derivative which indicated that all the six carbon and six hydrogen atoms of benzene are identical. On the basis of this observation August Kekulé in 1865 proposed the following structure for benzene having cyclic arrangement of six carbon atoms with alternate single and double bonds and one hydrogen atom attached to each carbon
atom.



FRIEDRICH AUGUST

KEKULÉ

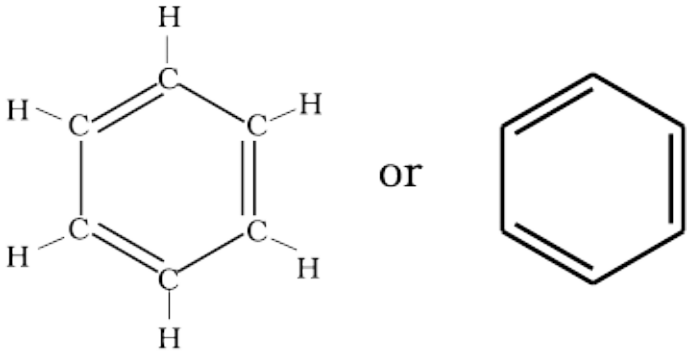
(7th September 1829–13th July 1896)

Friedrich August Kekulé,a German chemist was born in 1829 at Darmsdt in Germany. He became Professor in 1856 and Fellow of Royal Society in 1875. He made major contribution to structural organic chemistry by proposing in 1858 that carbon atoms can join to one another to form chains and later in 1865,he found an answer to the challenging problem of benzene structure by suggesting that these chains can close to form rings. He gave the dynamic structural formula to benzene which forms the basis for its modern electronic structure. He described the discovery of benzene structure later as:

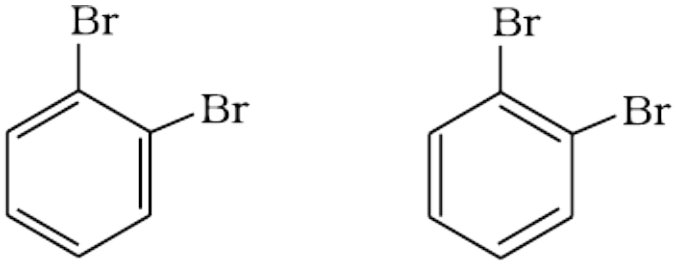
“I was sitting writing at my textbook,but the work did not progress; my thoughts were elsewhere. I turned my chair to the fire, and dozed. Again the atoms were gambolling before my eyes. This time the smaller groups kept modestly in the background. My mental eye,

rendered more acute by repeated visions of this kind, could now distinguish larger structures of manifold conformations; long rows,sometimes more closely fitted together; all twisting and turning in snake like motion. But look! What was that? One of the snakes had seized hold of it's own tail, and the form whirled mockingly before my eyes. As if by a flash of lightning I woke;.... I spent the rest of the night working out the consequences of the hypothesis. Let us learn to dream, gentlemen, and then perhaps we shall learn the truth but let us beware of making our dreams public before they have been approved by the waking mind."(1890).

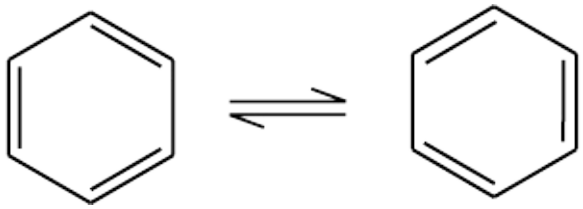
One hundred years later, on the occasion of Kekulé's centenary celebrations a group of compounds having polybenzenoid structures have been named as Kekulenes.



The Kekulé structure indicates the possibility of two isomeric 1, 2-dibromobenzenes. In one of the isomers, the bromine atoms are attached to the doubly bonded carbon atoms whereas in the other, they are attached to the singly bonded carbons.



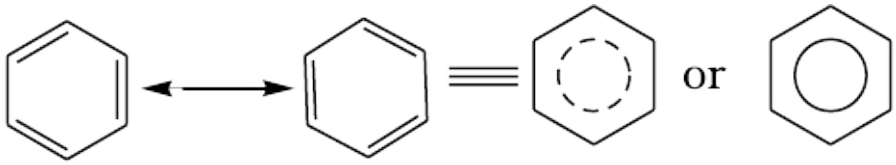
However, benzene was found to form only one ortho disubstituted product. This problem was overcome by Kekulé by suggesting the concept of oscillating nature of double bonds in benzene as given below.



Even with this modification, Kekulé structure of benzene fails to explain unusual stability and preference to substitution reactions than addition reactions, which could later on be explained by resonance.

Resonance and stability of benzene

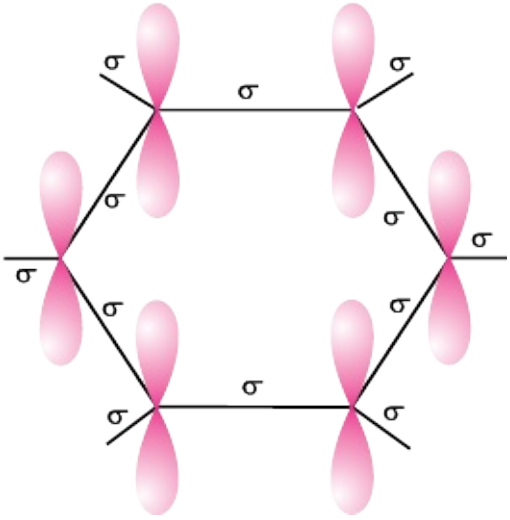
According to Valence Bond Theory, the concept of oscillating double bonds in benzene is now explained by resonance. Benzene is a hybrid of various resonating structures. The two structures, A and B given by Kekulé are the main contributing structures. The hybrid structure is represented by inserting a circle or a dotted circle in the hexagon as shown in (C). The circle represents the six electrons which are delocalised between the six carbon atoms of the benzene ring.



(A) (B) (C)

The orbital overlapping gives us better picture about the structure of benzene. All the six carbon atoms in benzene are sp2 hybridized. Two sp2 hybrid orbitals of each carbon atom overlap with sp2 hybrid orbitals of adjacent carbon atoms to form six C—C sigma bonds which are in the hexagonal plane. The remaining sp2 hybrid orbital of each carbon atom overlaps with s orbital of a hydrogen atom to form six C—H sigma bonds.

Each carbon atom is now left with one unhybridised p orbital perpendicular to the plane of the ring as shown below:



The unhybridised p orbital of carbon atoms are close enough to form a π bond by lateral overlap. There are two equal possibilities of forming three π bonds by overlap of p orbitals of C_1 –C_2, C_3 – C_4, C_5 – C_6 or C_2 – C_3, C_4 – C_5, C_6 – C_1 respectively as shown in the following figures.

Structures shown in Fig. 13.7(a) and (b) correspond to two Kekulé's structure with localised π bonds. The internuclear distance between all the carbon atoms in the ring has been determined by the X-ray diffraction to be the same; there is equal probability for the p orbital of each carbon atom to overlap with the p orbitals of adjacent carbon atoms [Fig. 13.7 (c)]. This can be represented in the form of two doughtnuts (rings) of electron clouds [Fig. 13.7 (d)], one above and one below the plane of the hexagonal ring as shown below:

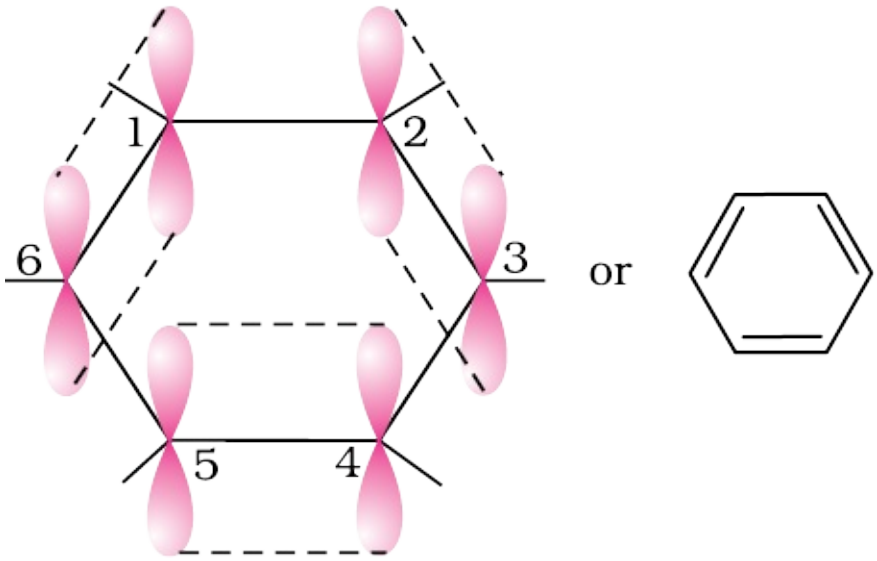


Fig. 13.7 (a)

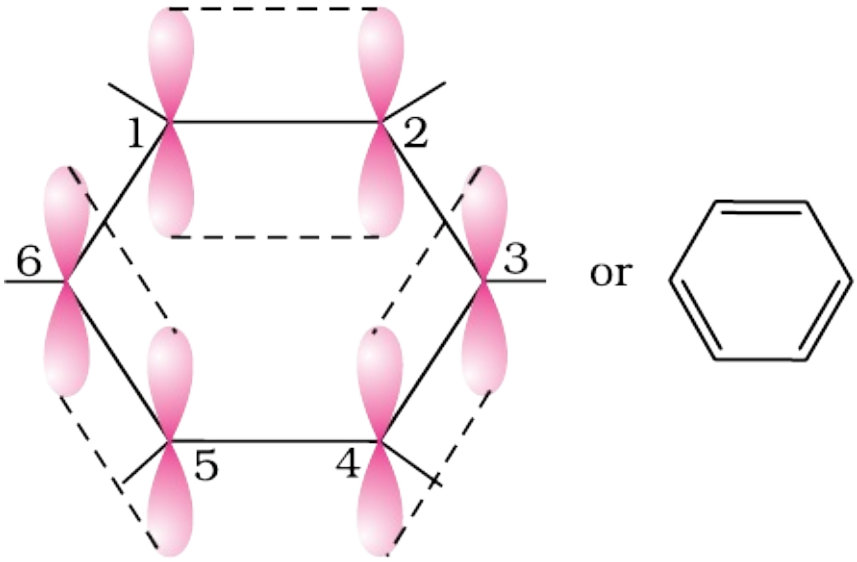


Fig. 13.7 (b)

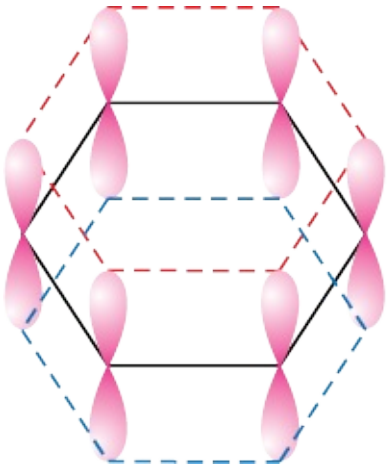


Fig. 13.7 (c)

or



Fig. 13.7 (d)

The six π electrons are thus delocalised and can move freely about the six carbon nuclei, instead of any two as shown in Fig. 13.6 (a) or (b). The delocalised π electron cloud is attracted more strongly by the nuclei of the carbon atoms than the electron cloud localised between two carbon atoms. Therefore, presence of delocalised π electrons in benzene makes it more stable than the hypothetical cyclohexatriene.

(electron cloud)

X-Ray diffraction data reveals that benzene is a planar molecule. Had any one of the above structures of benzene (A or B) been correct, two types of C—C bond lengths were expected. However, X-ray data indicates that all the six C—C bond lengths are of the same order (139 pm) which is intermediate between C— C single bond (154 pm) and C— C double bond (133 pm). Thus the absence of pure double bond in benzene accounts for the reluctance of benzene to show addition reactions under normal conditions, thus explaining the unusual behaviour of benzene.

13.5.3 Aromaticity

Benzene was considered as parent ‘aromatic’ compound. Now, the name

is applied to all the ring systems whether or not having benzene ring, possessing following characteristics.

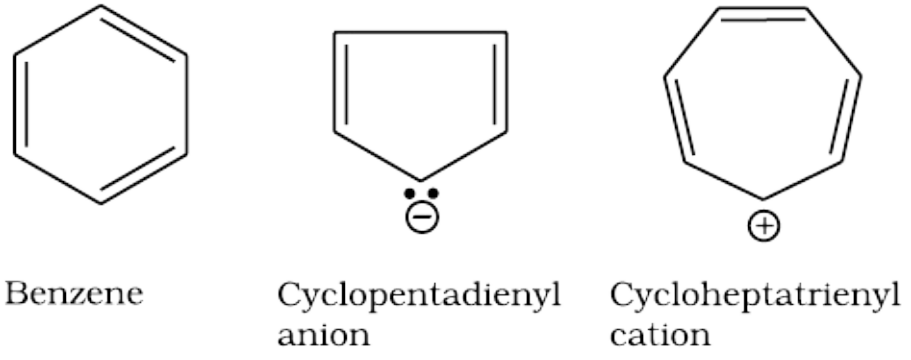
(i) Planarity

(ii) Complete delocalisation of the π electrons in the ring

(iii) Presence of (4n + 2) π electrons in the ring where n is an integer (n = 0, 1, 2, . . .).

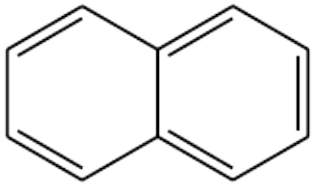
This is often referred to as **Hückel Rule**.

Some examples of aromatic compounds are given below:



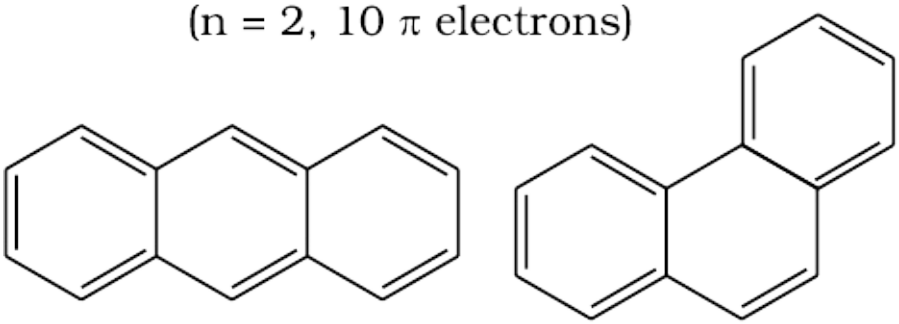
Benzene | Cyclopentadienyl anion | Cycloheptatrienyl cation

(n=1, 6π electrons)



Naphthalene

(n = 2, 10 π electrons)



Anthracene | Phenanthrene

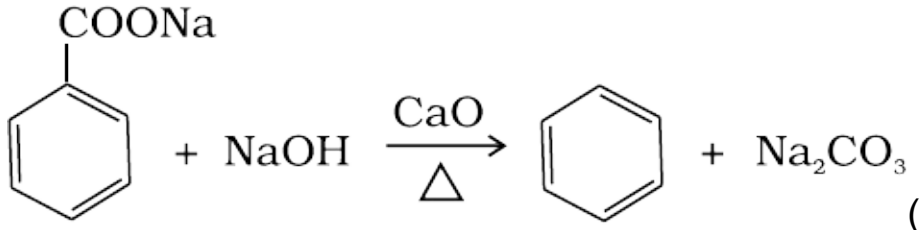
(n =3, 14 π electrons)

13.5.4 Preparation of Benzene

Benzene is commercially isolated from coal tar. However, it may be prepared in the laboratory by the following methods.

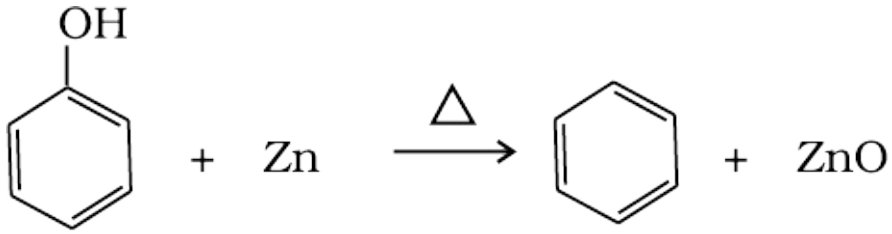
(i) ***Cyclic polymerisation of ethyne:*** (Section 13.4.4)

(ii) ***Decarboxylation of aromatic acids:*** Sodium salt of benzoic acid on heating with sodalime gives benzene.



(13.70)

(iii) Reduction of phenol: Phenol is reduced to benzene by passing its vapours over heated zinc dust



(13.71)

13.5.5 Properties

Physical properties

Aromatic hydrocarbons are non- polar molecules and are usually colourless liquids or solids with a characteristic aroma. You are also familiar with naphthalene balls which are used in toilets and for preservation of clothes because of unique smell of the compound and the

moth repellent property. Aromatic hydrocarbons are immiscible with water but are readily miscible with organic solvents. They burn with sooty flame.

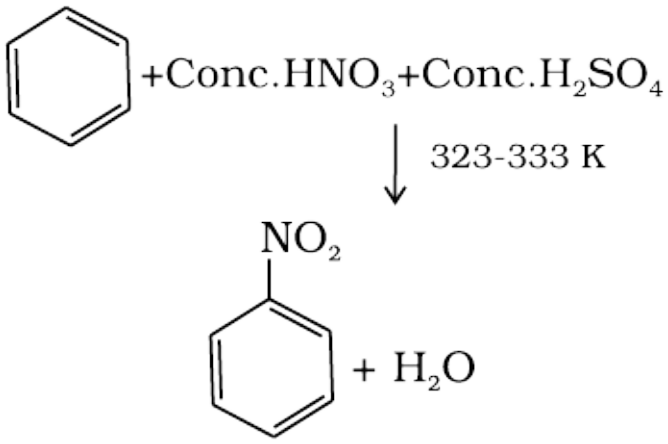
Chemical properties

Arenes are characterised by electrophilic substitution reactions. However, under special conditions they can also undergo addition and oxidation reactions.

Electrophilic substitution reactions

The common electrophilic substitution reactions of arenes are nitration, halogenation, sulphonation, Friedel Craft's alkylation and acylation reactions in which attacking reagent is an electrophile (E+)

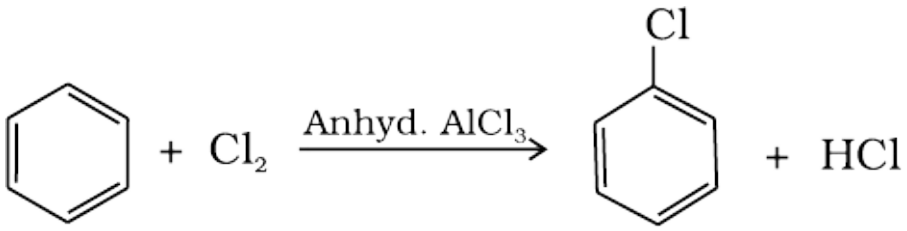
(i) Nitration: A nitro group is introduced into benzene ring when benzene is heated with a mixture of concentrated nitric acid and concentrated sulphuric acid (nitrating mixture).



(13.72)

Nitrobenzene

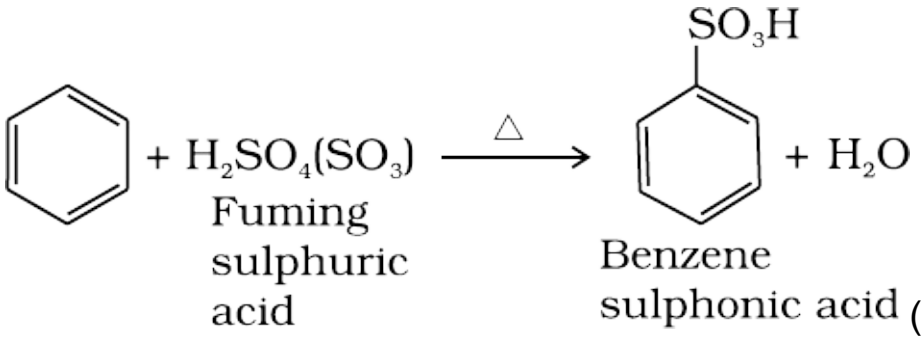
(ii) Halogenation: Arenes react with halogens in the presence of a Lewis acid like anhydrous $FeCl_3$, $FeBr_3$ or $AlCl_3$ to yield haloarenes.



Chlorobenzene

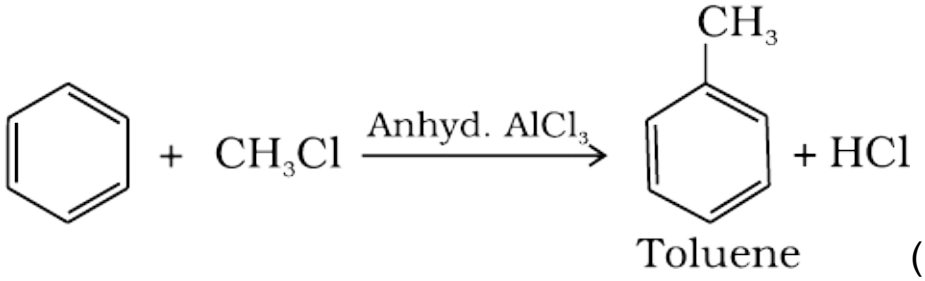
(13.73)

(iii) Sulphonation: The replacement of a hydrogen atom by a sulphonic acid group in a ring is called sulphonation. It is carried out by heating benzene with fuming sulphuric acid (oleum).

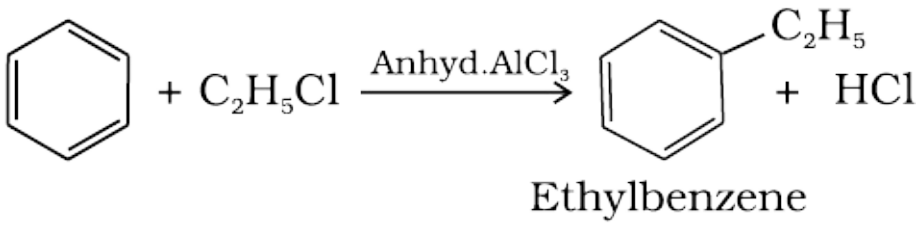


(13.74)

(iv) Friedel-Crafts alkylation reaction: When benzene is treated with an alkyl halide in the presence of anhydrous aluminium chloride, alkylbenene is formed.



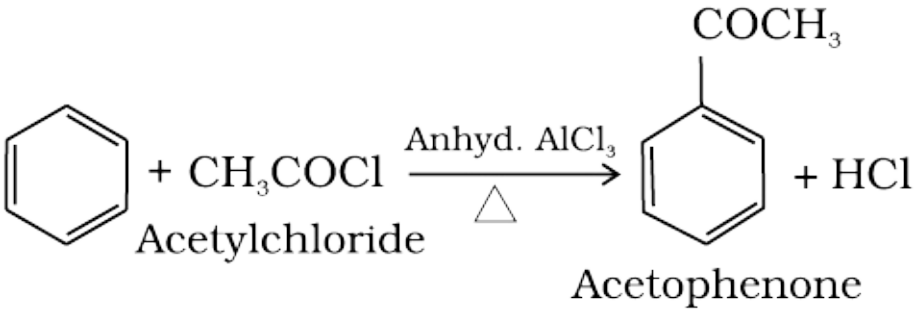
(13.75)



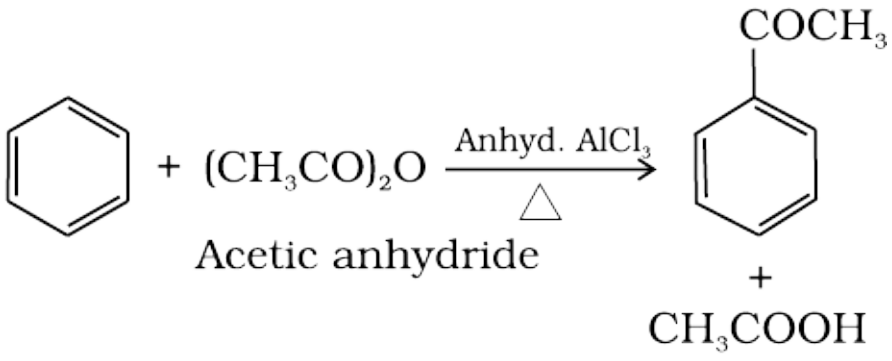
(13.76)

Why do we get isopropyl benzene on treating benzene with 1-chloropropane instead of n-propyl benzene?

(v) Friedel-Crafts acylation reaction: The reaction of benzene with an acyl halide or acid anhydride in the presence of Lewis acids ($AlCl_3$) yields acyl benzene.



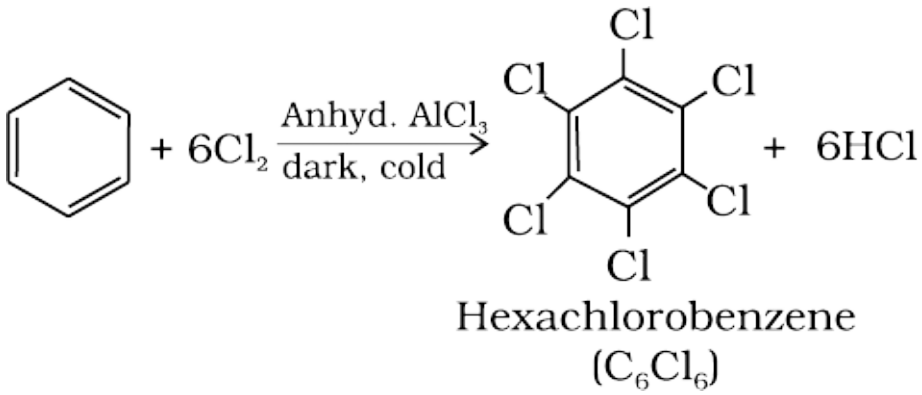
(13.77)



(13.78)

If excess of electrophilic reagent is used, further substitution reaction may take place in which other hydrogen atoms of benzene ring may also be successively replaced by the electrophile. For example, benzene on treatment with excess of chlorine in the presence of anhydrous AlCl3 can

be chlorinated to hexachlorobenzene (C_6Cl_6)



(13.79)

Mechanism of electrophilic substitution reactions:

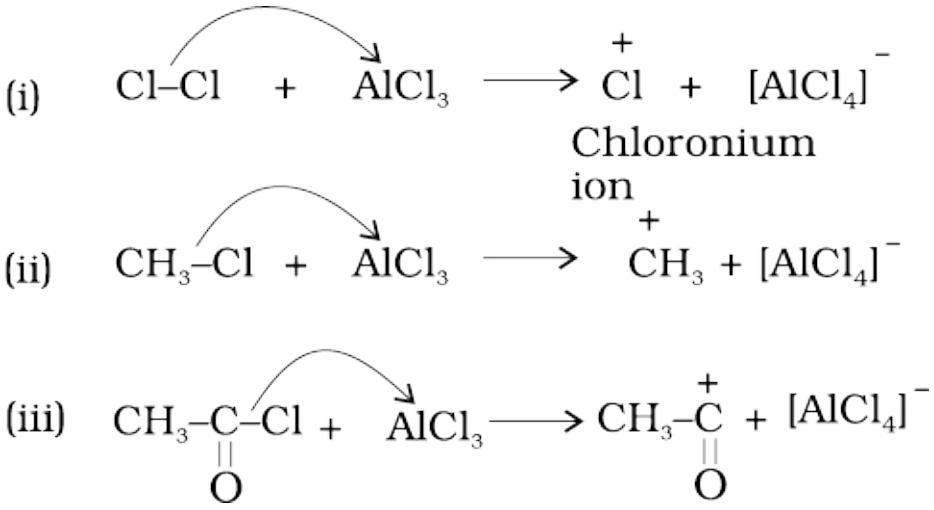
According to experimental evidences, SE (S = substitution; E = electrophilic) reactions are supposed to proceed via the following three steps:

(a) Generation of the eletrophile

(b) Formation of carbocation intermediate

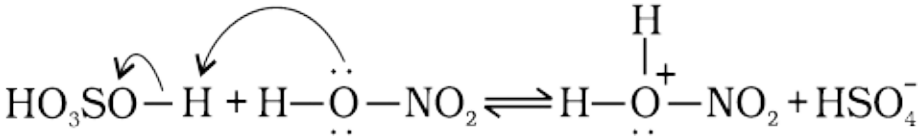
(c) Removal of proton from the carbocation intermediate

(a) Generation of electrophile E⊕: During chlorination, alkylation and acylation of benzene, anhydrous $AlCl_3$, being a Lewis acid helps in generation of the elctrophile Cl⊕, R⊕, RC⊕O (acylium ion) respectively by combining with the attacking reagent.

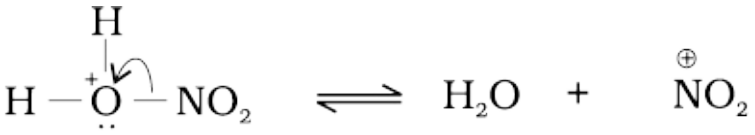


In the case of nitration, the electrophile, nitronium ion, $\overset{+}{N}O_2$ is produced by transfer of a proton (from sulphuric acid) to nitric acid in the following manner:

Step I



Step II

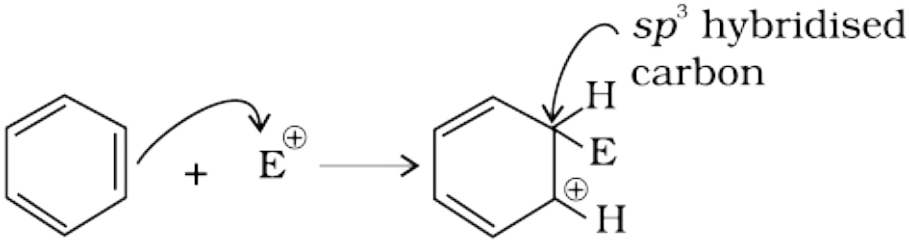


Protonated Nitronium nitric acid ion

It is interesting to note that in the process of generation of nitronium ion, sulphuric acid serves as an acid and nitric acid as a base. Thus, it is a simple acid-base equilibrium.

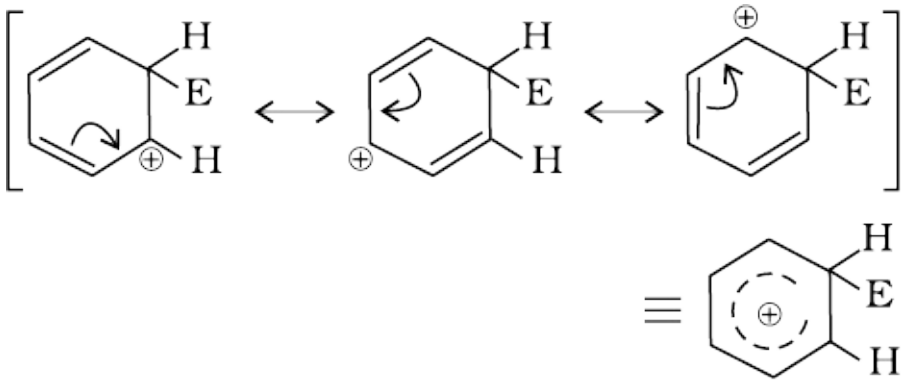
(b) Formation of Carbocation (arenium ion): Attack of electrophile

results in the formation of σ-complex or arenium ion in which one of the carbon is sp3 hybridised.



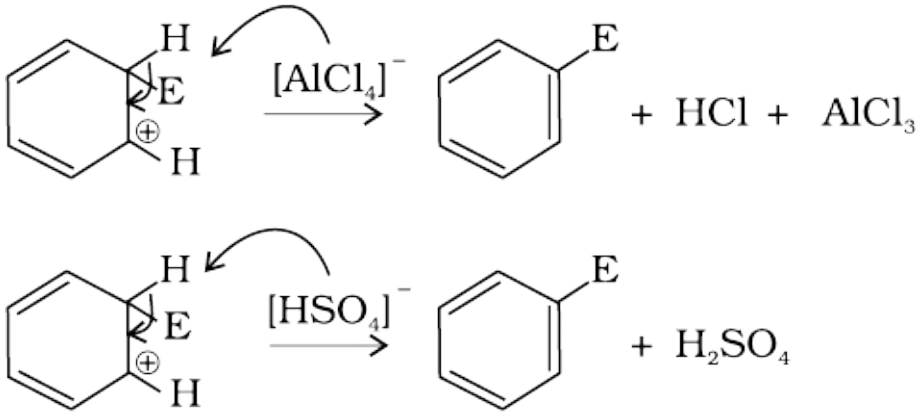
sigma complex (arenium ion)

The arenium ion gets stabilised by resonance:



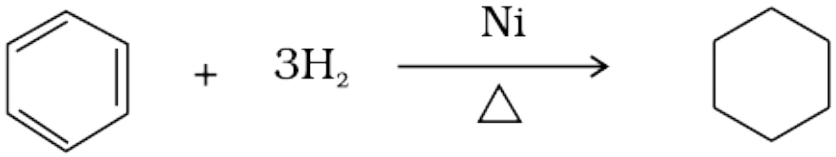
Sigma complex or arenium ion loses its aromatic character because delocalisation of electrons stops at sp3 hybridised carbon.

(c) Removal of proton: To restore the aromatic character, σ -complex releases proton from sp3 hybridised carbon on attack by [AlCl4]– (in case of halogenation, alkylation and acylation) and [HSO4]– (in case of nitration).



Addition reactions

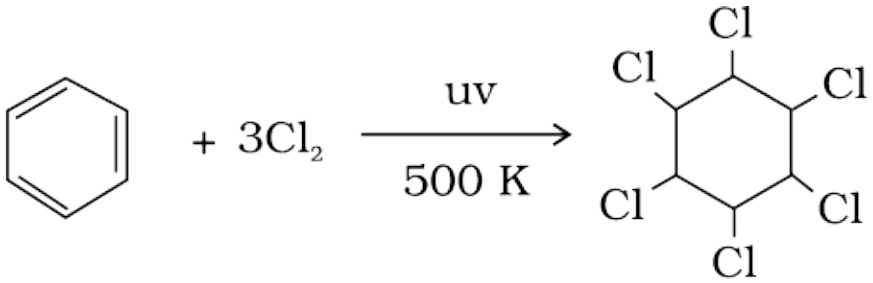
Under vigorous conditions, i.e., at high temperature and/ or pressure in the presence of nickel catalyst, hydrogenation of benzene gives cyclohexane.



Cyclohexane

(13.80)

Under ultra-violet light, three chlorine molecules add to benzene to produce benzene hexachloride, C6H6Cl6 which is also called gammaxane.



Benzene hexachloride, (BHC)

(13.81)

Combustion: When heated in air, benzene burns with sooty flame producing CO2 and H2O

$$C_6H_6 + \frac{15}{2}O_2 \rightarrow 6CO_2 + 3H_2O \quad (13.82)$$

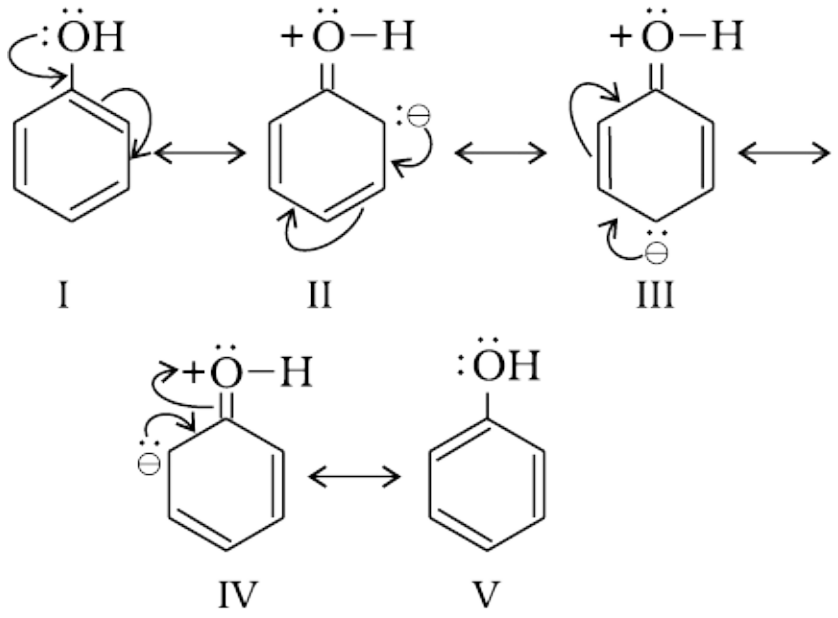
General combustion reaction for any hydrocarbon may be given by the following chemical equation:

$$CxHy + (x + \frac{y}{4}) O2 \rightarrow x\ CO2 + \frac{y}{2}\ H2O \quad (13.83)$$

13.5.6 Directive influence of a functional group in monosubstituted benzene

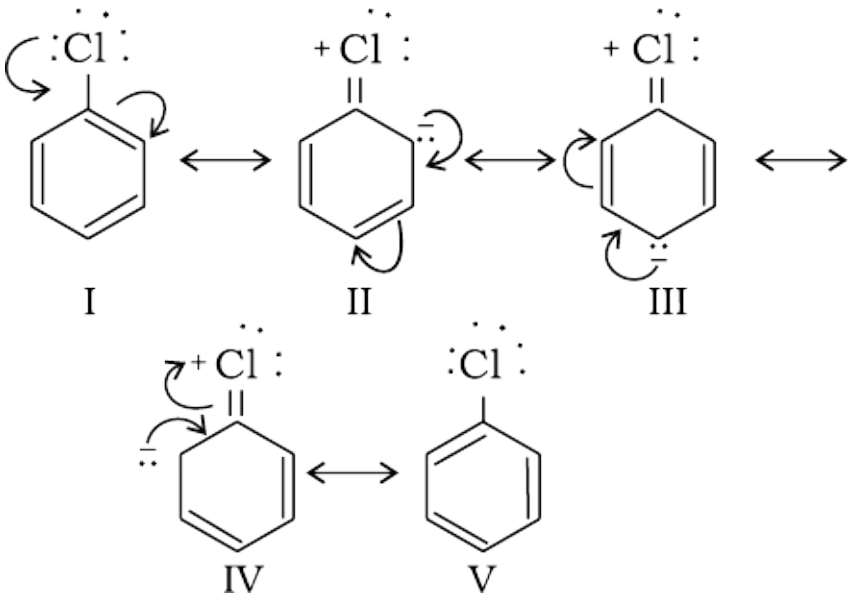
When monosubstituted benzene is subjected to further substitution, three possible disubstituted products are not formed in equal amounts. Two types of behaviour are observed. Either ortho and para products or meta product is predominantly formed. It has also been observed that this behaviour depends on the nature of the substituent already present in the benzene ring and not on the nature of the entering group. This is known as directive influence of substituents. Reasons for ortho/para or meta directive nature of groups are discussed below:

Ortho and para directing groups: The groups which direct the incoming group to ortho and para positions are called ortho and para directing groups. As an example, let us discuss the directive influence of phenolic (–OH) group. Phenol is resonance hybrid of following structures:



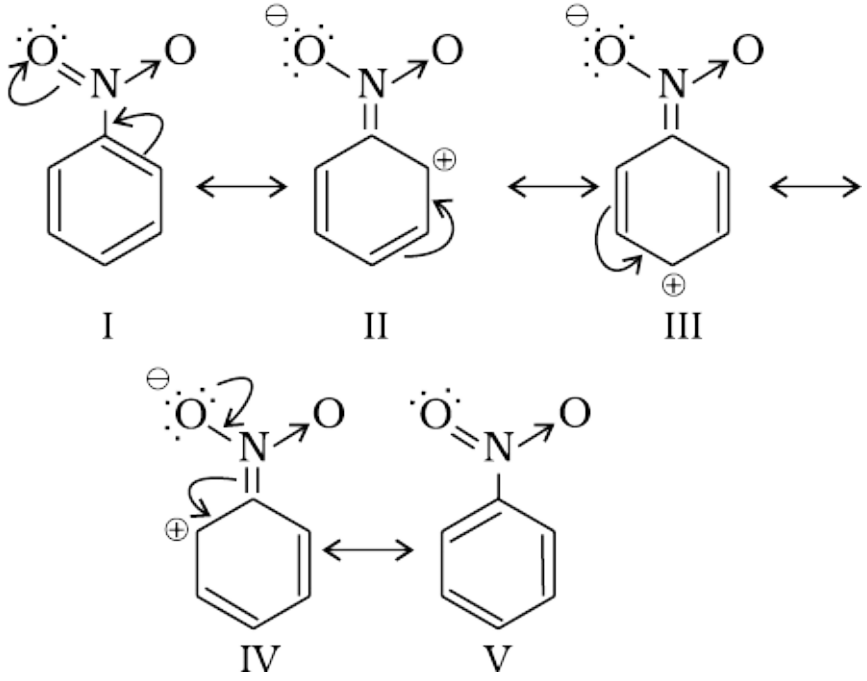
It is clear from the above resonating structures that the electron density is more on o – and p – positions. Hence, the substitution takes place mainly at these positions. However, it may be noted that –I effect of – OH group also operates due to which the electron density on ortho and para positions of the benzene ring is slightly reduced. But the overall electron density increases at these positions of the ring due to resonance. Therefore, –OH group activates the benzene ring for the attack by an electrophile. Other examples of **activating** groups are $–NH_2$, –NHR, $–NHCOCH_3$, $–OCH_3$, $–CH_3$, $–C_2H_5$, etc.

In the case of aryl halides, halogens are moderately **deactivating**. Because of their strong – I effect, overall electron density on benzene ring decreases. It makes further substitution difficult. However, due to resonance the electron density on o– and p– positions is greater than that at the m-position. Hence, they are also o– and p– directing groups. Resonance structures of chlorobenzene are given below:



Meta directing group: The groups which direct the incoming group to meta position are called meta directing groups. Some examples of meta directing groups are $–NO_2$, –CN, –CHO, –COR, –COOH, –COOR, $–SO_3H$, etc.

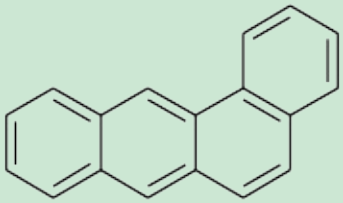
Let us take the example of nitro group. Nitro group reduces the electron density in the benzene ring due to its strong–I effect. Nitrobenzene is a resonance hybrid of the following structures.



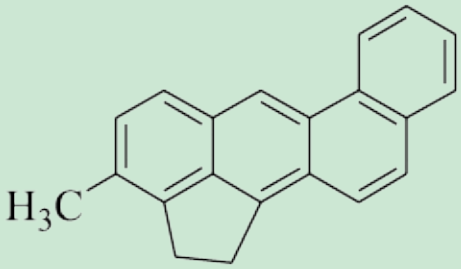
In this case, the overall electron density on benzene ring decreases making further substitution difficult, therefore these groups are also called ‘deactivating groups’. The electron density on o– and p– position is comparatively less than that at meta position. Hence, the electrophile attacks on comparatively electron rich meta position resulting in meta substitution.

13.6 CARCINOGENICITY AND TOXICITY

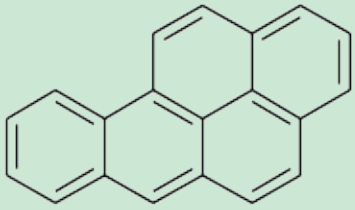
Benzene and polynuclear hydrocarbons containing more than two benzene rings fused together are toxic and said to possess cancer producing (carcinogenic) property. Such polynuclear hydrocarbons are formed on incomplete combustion of organic materials like tobacco, coal and petroleum. They enter into human body and undergo various biochemical reactions and finally damage DNA and cause cancer. Some of the carcinogenic hydrocarbons are given below (see box).



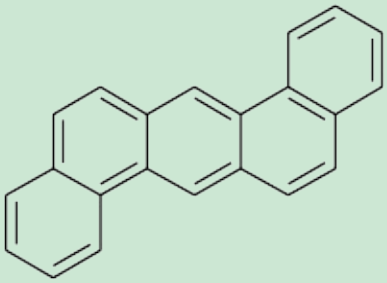
1,2-Benzanthracene



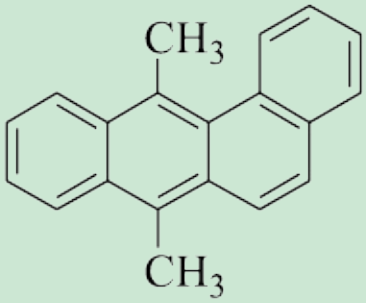
3-Methylcholanthrene



1,2-Benzpyrene



1,2,5,6-Dibenzanthracene



9,10-Dimethyl-1,2-benzanthracene

SUMMARY

Hydrocarbons are the compounds of carbon and hydrogen only. Hydrocarbons are mainly obtained from coal and petroleum, which are the major sources of energy. Petrochemicals are the prominent

starting materials used for the manufacture of a large number of commercially important products. LPG (liquefied petroleum gas) and CNG (compressed natural gas), the main sources of energy for domestic fuels and the automobile industry, are obtained from petroleum. Hydrocarbons are classified as open chain saturated (alkanes) and unsaturated (alkenes and alkynes), cyclic (alicyclic) and aromatic, according to their structure.

The important reactions of alkanes are free radical substitution, combustion, oxidation and aromatization. Alkenes and alkynes undergo addition reactions, which are mainly electrophilic additions. Aromatic hydrocarbons, despite having unsaturation, undergo mainly electrophilic substitution reactions. These undergo addition reactions only under special conditions.

Alkanes show conformational isomerism due to free rotation along the C–C sigma bonds. Out of staggered and the eclipsed conformations of ethane, staggered conformation is more stable as hydrogen atoms are farthest apart. Alkenes exhibit geometrical (cis-trans) isomerism due to restricted rotation around the carbon–carbon double bond.

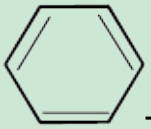
Benzene and benzenoid compounds show aromatic character. Aromaticity, the property of being aromatic is possessed by compounds having specific electronic structure characterised by Hückel $(4n+2)\pi$ electron rule. The nature of groups or substituents attached to benzene ring is responsible for activation or deactivation of the benzene ring towards further electrophilic substitution and also for orientation of the incoming group. Some of the polynuclear hydrocarbons having fused benzene ring system have carcinogenic property.

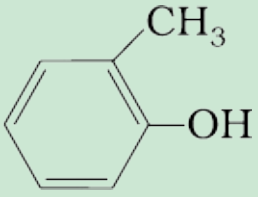
EXERCISES

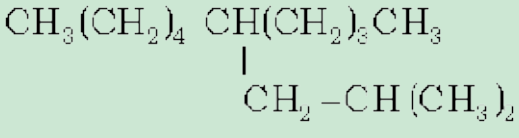
13.1 How do you account for the formation of ethane during chlorination of methane ?

13.2 Write IUPAC names of the following compounds :

(a) $CH_3CH=C(CH_3)_2$ (b) $CH_2=CH-C\equiv C-CH_3$

(c)  (d)  $-CH_2-CH_2-CH=CH_2$

(e) 

(f) 

(g) $CH_3 - CH = CH - CH_2 - CH = CH - CH - CH_2 - CH = CH_2$

$$|$$

$$C_2H_5$$

13.3 For the following compounds, write structural formulas and IUPAC names for all possible isomers having the number of double or triple bond as indicated :

(a) C_4H_8 (one double bond) (b) C_5H_8 (one triple bond)

13.4 Write IUPAC names of the products obtained by the ozonolysis of the following compounds :

(i) Pent-2-ene (ii) 3,4-Dimethylhept-3-ene

(iii) 2-Ethylbut-1-ene (iv) 1-Phenylbut-1-ene

13.5 An alkene 'A' on ozonolysis gives a mixture of ethanal and pentan-3-one. Write structure and IUPAC name of 'A'.

13.6 An alkene 'A' contains three C – C, eight C – H σ bonds and one C – C π bond. 'A' on ozonolysis gives two moles of an aldehyde of molar mass 44 u. Write IUPAC name of 'A'.

13.7 Propanal and pentan-3-one are the ozonolysis products of an alkene? What is the structural formula of the alkene?

13.8 Write chemical equations for combustion reaction of the following hydrocarbons:

(i) Butane (ii) Pentene

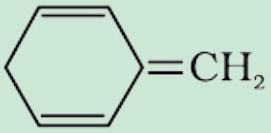
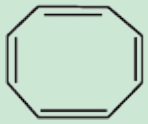
(iii) Hexyne (iv) Toluene

13.9 Draw the cis and trans structures of hex-2-ene. Which isomer will have higher b.p. and why?

13.10 Why is benzene extra ordinarily stable though it contains three double bonds?

13.11 What are the necessary conditions for any system to be aromatic?

13.12 Explain why the following systems are not aromatic?

(i)  (ii)  (iii) 

13.13 How will you convert benzene into

(i) p-nitrobromobenzene (ii) m- nitrochlorobenzene

(iii) p - nitrotoluene (iv) acetophenone?

13.14 In the alkane $H_3C - CH_2 - C(CH_3)_2 - CH_2 - CH(CH_3)_2$, identify 1°,2°,3° carbon atoms and give the number of H atoms bonded to each one of these.

13.15 What effect does branching of an alkane chain has on its boiling point?

13.16 Addition of HBr to propene yields 2-bromopropane, while in the presence of benzoyl peroxide, the same reaction yields 1-bromopropane. Explain and give mechanism.

13.17 Write down the products of ozonolysis of 1,2-dimethylbenzene (o-xylene). How does the result support Kekulé structure for benzene?

13.18 Arrange benzene, n-hexane and ethyne in decreasing order of acidic behaviour. Also give reason for this behaviour.

13.19 Why does benzene undergo electrophilic substitution reactions easily and nucleophilic substitutions with difficulty?

13.20 How would you convert the following compounds into benzene?

(i) Ethyne (ii) Ethene (iii) Hexane

13.21 Write structures of all the alkenes which on hydrogenation give 2-methylbutane.

13.22 Arrange the following set of compounds in order of their decreasing relative reactivity with an electrophile, E+

(a) Chlorobenzene, 2,4-dinitrochlorobenzene, p-nitrochlorobenzene

(b) Toluene, p-$H_3C - C_6H_4 - NO_2$, p-$O_2N - C_6H_4 - NO_2$.

13.23 Out of benzene, m–dinitrobenzene and toluene which will undergo nitration most easily and why?

13.24 Suggest the name of a Lewis acid other than anhydrous aluminium chloride which can be used during ethylation of benzene.

13.25 Why is Wurtz reaction not preferred for the preparation of alkanes containing odd number of carbon atoms? Illustrate your answer by taking one example.

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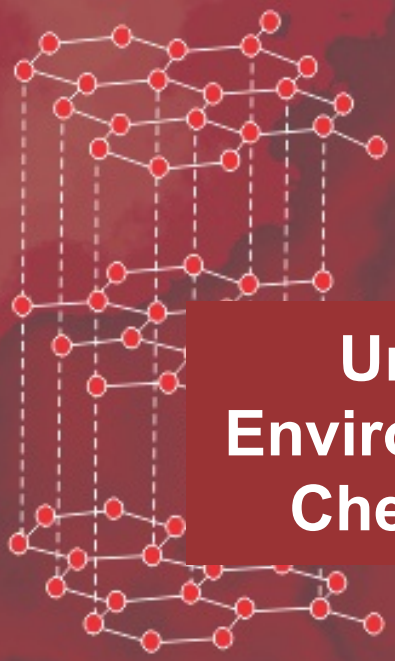
Electrophilic substitution reactions

Mechanism of electrophilic substitution reactions:

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13.5.6 Directive influence of a functional group in monosubstituted benzene
13.6 Carcinogenicity and Toxicity

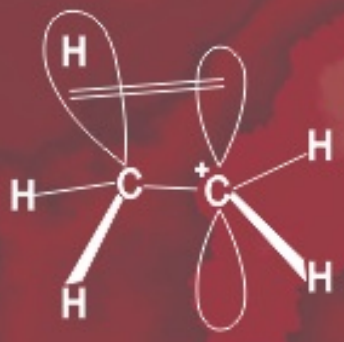
Textbook for Class XI



Unit 14
Environmental Chemistry

Chemistry

Part II



11083CH14

Unit 14

Environmental Chemistry

Objectives

After studying this unit, you will be able to

• understand the meaning of environmental chemistry;

• define atmospheric pollution, list reasons for global warming. green house effect and acid rain;

• identify causes for ozone layer depletion and its effects;

• give reasons for water pollution and know about international standards for drinking water;

• describe causes of soil pollution;

• suggest and adopt strategies for control of environmental pollution;

• appreciate the importance of green chemistry in day to day life.

*"**The world has achieved brilliance without wisdom, power without conscience. Ours is a world of nuclear giants and ethical infants.**"*

You have already studied about environment in your earlier classes. Environmental studies deal with the sum of all social, economical, biological, physical and chemical interrelations with our surroundings. In this unit the focus will be on environmental chemistry. Environmental chemistry deals with the study of the origin, transport, reactions, effects and fates of chemical species in the environment. Let us discuss some important aspects of environmental chemistry.

14.1 ENVIRONMENTAL POLLUTION

Environmental pollution is the effect of undesirable changes in our surroundings that have harmful effects on plants, animals and human beings. A substance, which causes pollution, is known as pollutant. Pollutants can be solid, liquid or gaseous substances present in greater concentration than in natural abundance and are produced due to human activities or due to natural happenings. Do you know, an average human being requires nearly 12-15 times more air than the food. So, even small amounts of pollutants in the air become significant compared to similar levels present in the food. Pollutants can be degradable, like discarded vegetables which rapidly break down by natural processes. On the other hand, pollutants which are slowly degradable, remain in the environment in an unchanged form for many decades. For example, substances such as dichlorodi-phenyltrichloroethane (DDT), plastic materials, heavy metals, many chemicals, nuclear wastes etc., once released into the environment are difficult to remove. These pollutants cannot be degraded by natural processes and are harmful to living organisms. In the process

of environmental pollution, pollutants originate from a source and get transported by air or water or are dumped into the soil by human beings.

14.2 ATMOSPHERIC POLLUTION

The atmosphere that surrounds the earth is not of the same thickness at all heights. There are concentric layers of air or regions and each layer has different density. The lowest region of atmosphere in which the human beings along with other organisms live is called troposphere. It extends up to the height of
~ 10 km from sea level. Above the troposphere, between 10 and 50 km above sea level lies stratosphere. Troposphere is a turbulent, dusty zone containing air, much water vapour and clouds. This is the region of strong air movement and cloud formation. The stratosphere, on the other hand, contains dinitrogen, dioxygen, ozone and little water vapour.

Atmospheric pollution is generally studied as tropospheric and stratospheric pollution. The presence of ozone in the stratosphere prevents about 99.5 per cent of the sun's harmful ultraviolet (UV) radiations from reaching the earth's surface and thereby protecting humans and other animals from its effect.

14.2.1 Tropospheric Pollution

Tropospheric pollution occurs due to the presence of undesirable solid or gaseous particles in the air. The following are the major gaseous and particulate pollutants present in the troposphere:

1. Gaseous air pollutants: These are oxides of sulphur, nitrogen and carbon, hydrogen sulphide, hydrocarbons, ozone and other oxidants.

2. Particulate pollutants: These are dust, mist, fumes, smoke, smog etc.

1. Gaseous air pollutants

(a) Oxides of Sulphur: Oxides of sulphur are produced when sulphur containing fossil fuel is burnt. The most common species, sulphur dioxide, is a gas that is poisonous to both animals and plants. It has been reported that even a low concentration of sulphur dioxide causes respiratory diseases e.g., asthma, bronchitis, emphysema in human beings. Sulphur dioxide causes irritation to the eyes, resulting in tears and redness. High concentration of SO2 leads to stiffness of flower buds which eventually fall off from plants. Uncatalysed oxidation of sulphur dioxide is slow. However, the presence of particulate matter in polluted air catalyses the oxidation of sulphur dioxide to sulphur trioxide.

$$2SO_2\,(g) + O_2\,(g) \rightarrow 2SO_3(g)$$

The reaction can also be promoted by ozone and hydrogen peroxide.

$$SO_2\,(g) + O_3\,(g) \rightarrow SO_3(g) + O_2\,(g)$$

$$SO_2(g) + H_2O_2(l) \rightarrow H_2SO_4(aq)$$

(b) Oxides of Nitrogen: Dinitrogen and dioxygen are the main constituents of air. These gases do not react with each other at a normal temperature. At high altitudes when lightning strikes, they combine to form oxides of nitrogen. NO_2 is oxidised to nitrate ion, NO_3^- which is washed into soil, where it serves as a fertilizer. In an automobile engine, (at high temperature) when fossil fuel is burnt, dinitrogen and dioxygen combine to yield significant quantities of nitric oxide (NO) and nitrogen dioxide (NO_2) as given below:

$$N2\,(g) + O2\,(g) \xrightarrow{1483K} 2NO(g)$$

NO reacts instantly with oxygen to give NO_2

$$2NO\ (g) + O_2\ (g) \rightarrow 2NO_2\ (g)$$

Rate of production of NO_2 is faster when nitric oxide reacts with ozone in the stratosphere.

$$NO\ (g) + O_3\ (g) \rightarrow NO_2\ (g) + O_2\ (g)$$

The irritant red haze in the traffic and congested places is due to oxides of nitrogen. Higher concentrations of NO_2 damage the leaves of plants and retard the rate of photosynthesis. Nitrogen dioxide is a lung irritant that can lead to an acute respiratory disease in children. It is toxic to living tissues also. Nitrogen dioxide is also harmful to various textile fibres and metals.

(c) Hydrocarbons: Hydrocarbons are composed of hydrogen and carbon only and are formed by incomplete combustion of fuel used in automobiles. Hydrocarbons are carcinogenic, i.e., they cause cancer. They harm plants by causing ageing, breakdown of tissues and shedding of leaves, flowers and twigs.

(d) Oxides of Carbon

(i) Carbon monoxide: Carbon monoxide (CO) is one of the most serious air pollutants. It is a colourless and odourless gas, highly poisonous to living beings because of its ability to block the delivery of oxygen to the organs and tissues. It is produced as a result of incomplete combustion of carbon. Carbon monoxide is mainly released into the air by automobile exhaust. Other sources, which produce CO, involve incomplete combustion of coal, firewood, petrol, etc. The number of vehicles has been increasing over the years all over the world. Many vehicles are poorly maintained and several have inadequate pollution control equipments resulting in the release of greater amount of carbon monoxide and other polluting gases. Do you know why carbon monoxide

is poisonous? It binds to haemoglobin to form carboxyhaemoglobin, which is about 300 times more stable than the oxygen-haemoglobin complex. In blood, when the concentration of carboxyhaemoglobin reaches about 3–4 per cent, the oxygen carrying capacity of blood is greatly
reduced. This oxygen deficiency, results into headache, weak eyesight, nervousness and cardiovascular disorder. This is the reason why people are advised not to smoke. In pregnant women who have the habit of smoking the increased CO level in blood may induce premature birth, spontaneous abortions and deformed babies.

(ii) Carbon dioxide: Carbon dioxide (CO_2) is released into the atmosphere by respiration, burning of fossil fuels for energy, and by decomposition of limestone during the manufacture of cement. It is also emitted during volcanic eruptions. Carbon dioxide gas is confined to troposphere only. Normally it forms about 0.03 per cent by volume of the atmosphere. With the increased use of fossil fuels, a large amount of carbon dioxide gets released into the atmosphere. Excess of CO_2 in the air is removed by green plants and this maintains an appropriate level of CO_2 in the atmosphere. Green plants require CO_2 for photosynthesis and they, in turn, emit oxygen, thus maintaining the delicate balance. As you know, deforestation and burning of fossil fuel increases the CO_2 level and disturb the balance in the atmosphere. The increased amount of CO_2 in the air is mainly responsible for global warming.

Global Warming and Greenhouse Effect

About 75 % of the solar energy reaching the earth is absorbed by the earth's surface, which increases its temperature. The rest of the heat radiates back to the atmosphere. Some of the heat is trapped by gases such as carbon dioxide, methane, ozone, chlorofluorocarbon compounds

(CFCs) and water vapour in the atmosphere. Thus, they add to the heating of the atmosphere. This causes global warming.

We all know that in cold places flowers, vegetables and fruits are grown in glass covered areas called greenhouse. Do you know that we humans also live in a greenhouse? Of course, we are not surrounded by glass but a blanket of air called the atmosphere, which has kept the temperature on earth constant for centuries. But it is now undergoing change, though slowly. Just as the glass in a greenhouse holds the sun's warmth inside, atmosphere traps the sun's heat near the earth's surface and keeps it warm. This is called natural greenhouse effect because it maintains the temperature and makes the earth perfect for life. In a greenhouse, solar radiations pass through the transparent glass and heat up the soil and the plants. The warm soil and plants emit infrared radiations. Since glass is opaque to infrared radiations (thermal region), it partly reflects and partly absorbs these radiations. This mechanism keeps the energy of the sun trapped in the greenhouse. Similarly, carbon dioxide molecules also trap heat as they are transparent to sunlight but not to the heat radiation. If the amount of carbon dioxide crosses the delicate proportion of 0.03 per cent, the natural greenhouse balance may get disturbed. Carbon dioxide is the major contributor to global warming.

Besides carbon dioxide, other greenhouse gases are methane, water vapour, nitrous oxide, CFCs and ozone. Methane is produced naturally when vegetation is burnt, digested or rotted in the absence of oxygen. Large amounts of methane are released in paddy fields, coal mines, from rotting garbage dumps and by fossil fuels. Chlorofluorocarbons (CFCs) are man-made industrial chemicals used in air conditioning etc. CFCs are also damaging the ozone layer (Section 14.2.2). Nitrous oxide occurs naturally in the environment. In recent years, their quantities have increased significantly due to the use of chemical fertilizers and the

burning of fossil fuels. If these trends continue, the average global temperature will increase to a level which may lead to melting of polar ice caps and flooding of low lying areas all over the earth. Increase in the global temperature increases the incidence of infectious diseases like dengue, malaria, yellow fever, sleeping sickness etc.

Think it Over

What can we do to reduce the rate of global warming?

If burning of fossil fuels, cutting down forests and trees add to greenhouse gases in the atmosphere, we must find ways to use these just efficiently and judiciously. One of the simple things which we can do to reduce global warming is to minimise the use of automobiles. Depending upon the situation, one can use bicycle, public transport system, or go for carpool. We should plant more trees to increase the green cover. Avoid burning of dry leaves, wood etc. It is illegal to smoke in public places and work places, because it is harmful not only for the one who is smoking but also for others, and therefore, we should avoid it. Many people do not understand the greenhouse effect and the global warming. We can help them by sharing the information that we have.

Acid rain

We are aware that normally rain water has a pH of 5.6 due to the presence of H+ ions formed by the reaction of rain water with carbon dioxide present in the atmosphere.

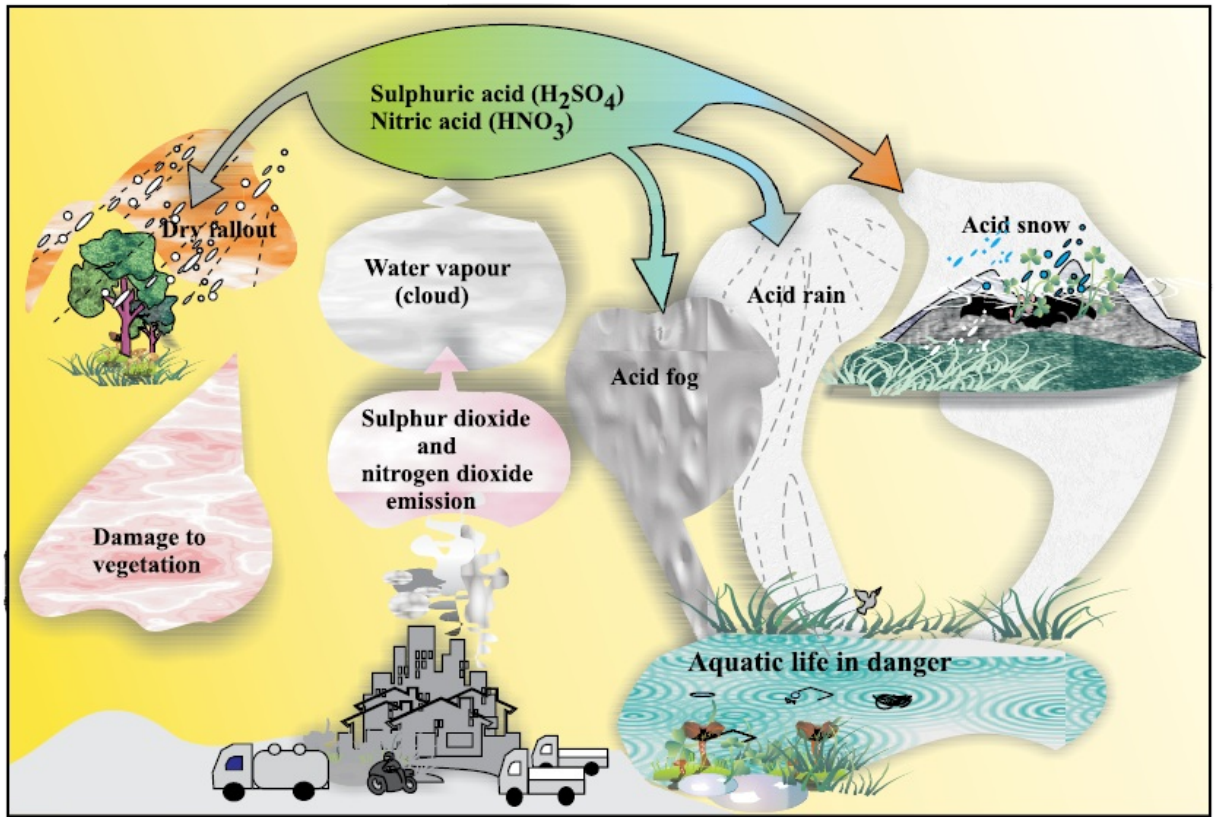


Fig. 14.1 Acid deposition

$$H_2O\ (l) + CO_2\ (g) \rightleftharpoons H_2CO_3\ (aq)$$

$$H_2CO_3\ (aq) \rightleftharpoons H^+(aq) + HCO_3^-(aq)$$

When the pH of the rain water drops below 5.6, it is called acid rain.

Acid rain refers to the ways in which acid from the atmosphere is deposited on the earth's surface. Oxides of nitrogen and sulphur which are acidic in nature can be blown by wind along with solid particles in the atmosphere and finally settle down either on the ground as dry deposition or in water, fog and snow as wet deposition. (Fig. 14.1)

Acid rain is a byproduct of a variety of human activities that emit the oxides of sulphur and nitrogen in the atmosphere. As mentioned earlier, burning of fossil fuels (which contain sulphur and nitrogenous matter) such as coal and oil in power stations and furnaces or petrol and diesel in

motor engines produce sulphur dioxide and nitrogen oxides. SO2 and NO2after oxidation and reaction with water are major contributors to acid rain, because polluted air usually contains particulate matter that catalyse the oxidation.

$$2SO_2\,(g) + O_2\,(g) + 2H_2O\,(l) \rightarrow 2H_2SO_4\,(aq)$$

$$4NO_2\,(g) + O_2\,(g) + 2H_2O\,(l) \rightarrow 4HNO_3\,(aq)$$

Ammonium salts are also formed and can be seen as an atmospheric haze (aerosol of fine particles). Aerosol particles of oxides or ammonium salts in rain drops result in wet-deposition. SO2 is also absorbed directly on both solid and liquid ground surfaces and is thus deposited as dry-deposition.

Acid rain is harmful for agriculture, trees and plants as it dissolves and washes away nutrients needed for their growth. It causes respiratory ailments in human beings and animals. When acid rain falls and flows as ground water to reach rivers, lakes etc. it affects plants and animal life in aquatic ecosystem. It corrodes water pipes resulting in the leaching of heavy metals such as iron, lead and copper into the drinking water. Acid rain damages buildings and other structures made of stone or metal. The Taj Mahal in India has been affected by acid rain.

Activity 1

You can collect samples of water from nearby places and record their pH values. Discuss your results in the class. Let us discuss how we can help to reduce the formation of acid rain.

This can be done by reducing the emission of sulphur dioxide and nitrogen dioxide in the atmosphere. We should use less vehicles driven by fossil fuels; use less sulphur content fossil fuels for power plants and industries. We should use natural gas which is a better fuel

than coal or use coal with less sulphur content. Catalytic converters must be used in cars to reduce the effect of exhaust fumes on the atmosphere. The main component of the converter is a ceramic honeycomb coated with precious metals — Pd, Pt and Rh. The exhaust gases containing unburnt fuel, CO and NOx, when pass through the converter at 573 K, are converted into CO_2 and N_2. We can also reduce the acidity of the soil by adding powdered limestone to neutralise the acidity of the soil. Many people do not know of acid rain and its harmful effects. We can make them aware by passing on this information and save the Nature.

Taj Mahal and Acid Rain

The air around the city of Agra, where the Taj Mahal is located, contains fairly high levels of sulphur and nitrogen oxides. It is mainly due to a large number of industries and power plants around the area. Use of poor quality of coal, kerosene and firewood as fuel for domestic purposes add up to this problem. The resulting acid rain reacts with marble, $CaCO_3$ of Taj Mahal ($CaCO_3 + H_2SO_4 \rightarrow CaSO_4 + H_2O + CO_2$) causing damage to this wonderful monument that has attracted people from around the world. As a result, the monument is being slowly disfigured and the marble is getting discoloured and lustreless. The Government of India announced an action plan in early 1995 to prevent the disfiguring of this historical monument. Mathura refinery has already taken suitable measures to check the emission of toxic gases.

This plan aims at clearing the air in the 'Taj Trapezium'– an area that includes the towns of Agra, Firozabad, Mathura and Bharatpur. Under this plan more than 2000 polluting industries lying inside the trapezium would switch over to the use of natural gas or liquefied petroleum gas instead of coal or oil. A new natural gas pipeline would bring more than half a million cubic metres of natural gas a day to this area. People living in the city will also be encouraged to use liquefied petroleum gas in place of coal, kerosene or firewood. Vehicles plying

on highways in the vicinity of Taj would be encouraged to use low sulphur content diesel.

2. Particulate Pollutants

Particulates pollutants are the minute solid particles or liquid droplets in air. These are present in vehicle emissions, smoke particles from fires, dust particles and ash from industries. Particulates in the atmosphere may be viable or non-viable. The viable particulates e.g., bacteria, fungi, moulds, algae etc., are minute living organisms that are dispersed in the atmosphere. Human beings are allergic to some of the fungi found in air. They can also cause plant diseases.

Non-viable particulates may be classified according to their nature and size as follows:

(a) Smoke particulates consist of solid or mixture of solid and liquid particles formed during combustion of organic matter. Examples are cigarette smoke, smoke from burning of fossil fuel, garbage and dry leaves, oil smoke etc.

(b) Dust is composed of fine solid particles (over 1μm in diameter), produced during crushing, grinding and attribution of solid materials. Sand from sand blasting, saw dust from wood works, pulverized coal, cement and fly ash from factories, dust storms etc., are some typical examples of this type of particulate emission.

(c) Mists are produced by particles of spray liquids and by condensation of vapours in air. Examples are sulphuric acid mist and herbicides and insecticides that miss their targets and travel through air and form mists.

(d) Fumes are generally obtained by the condensation of vapours during sublimation, distillation, boiling and several other chemical reactions.

Generally, organic solvents, metals and metallic oxides form fume particles.

The effect of particulate pollutants are largely dependent on the particle size. Air- borne particles such as dust, fumes, mist etc., are dangerous for human health. Particulate pollutants bigger than 5 microns are likely to lodge in the nasal passage, whereas particles of about 10 micron enter into lungs easily.

Lead used to be a major air pollutant emitted by vehicles. Leaded petrol used to be the primary source of air-borne lead emission in Indian cities. This problem has now been overcome by using unleaded petrol in most of the cities in India. Lead interferes with the development and maturation of red blood cells.

Smog

The word smog is derived from smoke and fog. This is the most common example of air pollution that occurs in many cities throughout the world. There are two types of smog:

(a) Classical smog occurs in cool humid climate. It is a mixture of smoke, fog and sulphur dioxide. Chemically it is a reducing mixture and so it is also called as reducing smog.

(b) Photochemical smog occurs in warm, dry and sunny climate. The main components of the photochemical smog result from the action of sunlight on unsaturated hydrocarbons and nitrogen oxides produced by automobiles and factories. Photochemical smog has high concentration of oxidising agents and is, therefore, called as oxidising smog.

Formation of photochemical smog

When fossil fuels are burnt, a variety of pollutants are emitted into the earth’s troposphere. Two of the pollutants that are emitted are

hydrocarbons (unburnt fuels) and nitric oxide (NO). When these pollutants build up to sufficiently high levels, a chain reaction occurs from their interaction with sunlight in which NO is converted into nitrogen dioxide (NO2). This NO2 in turn absorbs energy from sunlight and breaks up into nitric oxide and free oxygen atom (Fig. 14.2).

$$NO_2(g) \xrightarrow{h\nu} NO(g) + O(g) \quad (i)$$

Oxygen atoms are very reactive and combine with the O_2 in air to produce ozone.

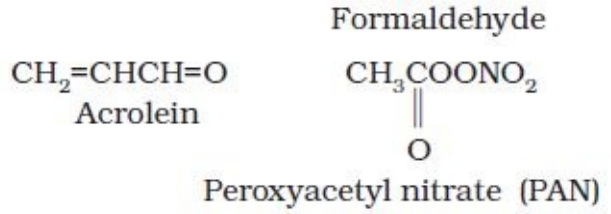
$$O(g) + O_2(g) \rightleftharpoons O_3(g) \quad (ii)$$

The ozone formed in the above reaction (ii) reacts rapidly with the NO(g) formed in the reaction (i) to regenerate NO_2. NO_2 is a brown gas and at sufficiently high levels can contribute to haze.

$$NO(g) + O_3(g) \rightarrow NO_2(g) + O_2(g) \quad (iii)$$

Ozone is a toxic gas and both NO_2 and O_3 are strong oxidising agents and can react with the unburnt hydrocarbons in the polluted air to produce chemicals such as formaldehyde, acrolein and peroxyacetyl nitrate (PAN).

$$3CH_4 + 2O_3 \rightarrow 3CH_2 = O + 3H_2O$$



Effects of photochemical smog

The common components of photochemical smog are ozone, nitric oxide, acrolein, formaldehyde and peroxyacetyl nitrate (PAN). Photochemical smog causes serious health problems. Both ozone and PAN act as powerful eye irritants. Ozone and nitric oxide irritate the nose and throat and their high concentration causes headache, chest pain, dryness of the throat, cough and difficulty in breathing. Photochemical smog leads to cracking of rubber and extensive damage to plant life. It also causes corrosion of metals, stones, building materials, rubber and painted surfaces.

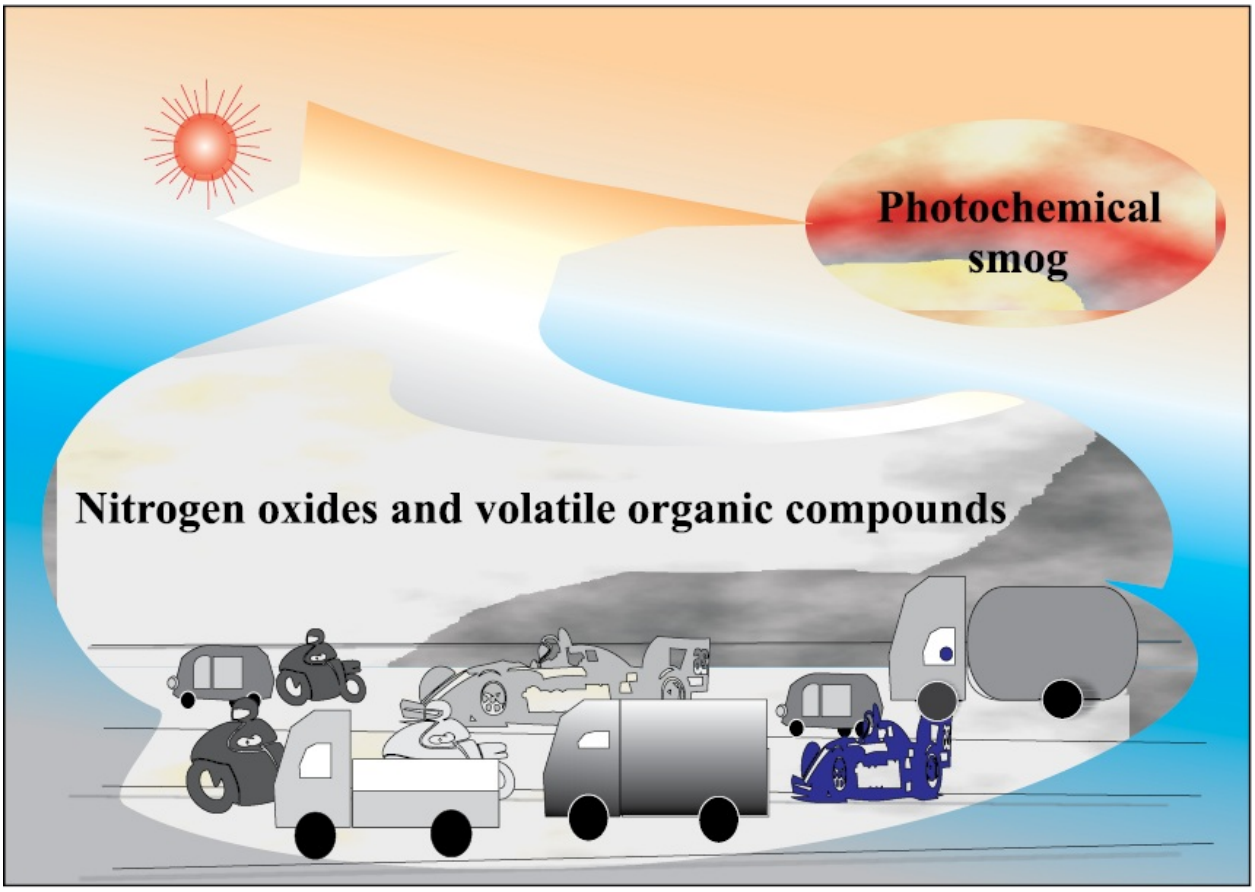


Fig. 14.2 Photochemical smog occurs where sunlight acts on vehicle pollutants.

How can photochemical smog be controlled ?

Many techniques are used to control or reduce the formation of

photochemical smog. If we control the primary precursors of photochemical smog, such as NO_2 and hydrocarbons, the secondary precursors such as ozone and PAN, the photochemical smog will automatically be reduced. Usually catalytic converters are used in the automobiles, which prevent the release of nitrogen oxide and hydrocarbons to the atmosphere. Certain plants e.g., Pinus, Juniparus, Quercus, Pyrus and Vitis can metabolise nitrogen oxide and therefore, their plantation could help in this matter.

14.2.2 Stratospheric Pollution

Formation and Breakdown of Ozone

The upper stratosphere consists of considerable amount of ozone (O_3), which protects us from the harmful ultraviolet (UV) radiations (λ 255 nm) coming from the sun. These radiations cause skin cancer (melanoma) in humans. Therefore, it is important to maintain the ozone shield.

Ozone in the stratosphere is a product of UV radiations acting on dioxygen (O_2) molecules. The UV radiations split apart molecular oxygen into free oxygen (O) atoms. These oxygen atoms combine with the molecular oxygen to form ozone.

$$O_2\,(g) \xrightarrow{UV} O(g) + O(g)$$

$$O(g) + O_2\,(g) \overset{UV}{\rightleftharpoons} O_3\,(g)$$

Ozone is thermodynamically unstable and decomposes to molecular oxygen. Thus, a dynamic equilibrium exists between the production and decomposition of ozone molecules. In recent years, there have been reports of the depletion of this protective ozone layer because of the presence of certain chemicals in the stratosphere. The main reason of

ozone layer depletion is believed to be the release of chlorofluorocarbon compounds (CFCs), also known as freons. These compounds are nonreactive, non flammable, non toxic organic molecules and therefore used in refrigerators, air conditioners, in the production of plastic foam and by the electronic industry for cleaning computer parts etc. Once CFCs are released in the atmosphere, they mix with the normal atmospheric gases and eventually reach the stratosphere. In stratosphere, they get broken down by powerful UV radiations, releasing chlorine free radical.

$$CF_2Cl_2\,(g) \xrightarrow{UV} \dot{C}l\,(g) + \dot{C}F_2Cl\,(g) \qquad (i)$$

The chlorine radical then react with stratospheric ozone to form chlorine monoxide radicals and molecular oxygen.

$$\dot{C}l\,(g) + O_3\,(g) \rightarrow Cl\dot{O}\,(g) + O_2\,(g) \qquad (ii)$$

Reaction of chlorine monoxide radical with atomic oxygen produces more chlorine radicals.

$$Cl\dot{O}\,(g) + O\,(g) \rightarrow \dot{C}l\,(g) + O_2\,(g) \qquad (iii)$$

The chlorine radicals are continuously regenerated and cause the breakdown of ozone. Thus, CFCs are transporting agents for continuously generating chlorine radicals into the stratosphere and damaging the ozone layer.

The Ozone Hole

In 1980s atmospheric scientists working in Antarctica reported about depletion of ozone layer commonly known as ozone hole over the South Pole. It was found that a unique set of conditions was responsible for the

ozone hole. In summer season, nitrogen dioxide and methane react with chlorine monoxide (reaction iv) and chlorine atoms (reaction v) forming chlorine sinks, preventing much ozone depletion, whereas in winter, special type of clouds called polar stratospheric clouds are formed over Antarctica. These polar stratospheric clouds provide surface on which chlorine nitrate formed (reaction iv) gets hydrolysed to form hypochlorous acid (reaction (vi)). It also reacts with hydrogen chloride produced as per reaction (v) to give molecular chlorine.

$$Cl\dot{O}\ (g) + NO_2\ (g) \rightarrow ClONO_2(g) \qquad \text{(iv)}$$

$$\dot{C}l\ (g) + CH_4\ (g) \rightarrow \dot{C}H3(g) + HCl(g) \qquad \text{(v)}$$

$$ClONO_2(g) + H_2O\ (g) \rightarrow HOCl\ (g) + HNO_3\ (g) \qquad \text{(vi)}$$

$$ClONO_2(g) + HCl\ (g) \rightarrow Cl_2\ (g) + HNO_3\ (g) \qquad \text{(vii)}$$

When sunlight returns to the Antarctica in the spring, the sun's warmth breaks up the clouds and HOCl and Cl_2 are photolysed by sunlight, as given in reactions (viii) and (ix).

$$HOCl\ (g) \xrightarrow{h\nu} \dot{O}H\ (g) + \dot{C}l(g) \qquad \text{(viii)}$$

$$Cl_2\ (g) \xrightarrow{h\nu} 2\dot{C}l\ (g) \qquad \text{(ix)}$$

The chlorine radicals thus formed, initiate the chain reaction for ozone depletion as described earlier.

Effects of Depletion of the Ozone Layer

With the depletion of ozone layer, more UV radiation filters into troposphere. UV radiations lead to ageing of skin, cataract, sunburn, skin cancer, killing of many phytoplanktons, damage to fish productivity etc. It

has also been reported that plant proteins get easily affected by UV radiations which leads to the harmful mutation of cells. It also increases evaporation of surface water through the stomata of the leaves and decreases the moisture content of the soil. Increase in UV radiations damage paints and fibres, causing them to fade faster.

14.3 WATER POLLUTION

Water is essential for life. Without water there would be no life. We usually take water as granted for its purity, but we must ensure the quality of water. Pollution of water originates from human activities. Through different paths, pollution reaches surface or ground water. Easily identified source or place of pollution is called as point source. e.g., municipal and industrial discharge pipes where pollutants enter the water-source. Non point sources of pollution are those where a source of pollution cannot be easily identified, e.g., agricultural run off (from farm, animals and crop-lands), acid rain, storm-water drainage (from streets, parking lots and lawns), etc. Table 14.1 lists the major water pollutants and their sources.

14.3.1 Causes of Water Pollution

(i) Pathogens: The most serious water pollutants are the disease causing agents called pathogens. Pathogens include bacteria and other organisms that enter water from domestic sewage and animal excreta. Human excreta contain bacteria such as Escherichia coli and Streptococcus faecalis which cause gastrointestinal diseases.

(ii) Organic wastes: The other major water pollutant is organic matter such as

leaves, grass, trash etc. They pollute water as a consequence of run off. Excessive phytoplankton growth within water is also a cause of water

pollution. These wastes are biodegradable.

The large population of bacteria decomposes organic matter present in water. They consume oxygen dissolved in water. The amount of oxygen that water can hold in the solution is limited. In cold water, dissolved oxygen (DO) can reach a concentration up to 10 ppm (parts per million), whereas oxygen in air is about 200,000 ppm. That is why even a moderate amount of organic matter when decomposes in water can deplete the water of its dissolved oxygen. The concentration of dissolved oxygen in water is very important for aquatic life . If the concentration of dissolved oxygen of water is below 6 ppm, the growth of fish gets inhibited. Oxygen reaches water either through atmosphere or from the process of photosynthesis carried out by many aquatic green plants during day light. However, during night, photosynthesis stops but the plants continue to respire, resulting in reduction of dissolved oxygen. The dissolved oxygen is also used by microorganisms to oxidise organic matter.

Table 14.1 Major Water Pollutants

Pollutant	Source
Micro-organisms	Domestic sewage
Organic wastes	Domestic sewage, animal excreta and waste, decaying animals and plants, discharge from food processing factories.
Plant nutrients	Chemcial fertilizers
Toxic heavy metals	Industries and chemical factories
Sediments	Erosion of soil by agriculture and strip mining
Pesticides	Chemicals used for killing insects, fungi and weeds
Radioactive substances	Mining of uranium containing minerals
Heat	Water used for cooling in industries

If too much of organic matter is added to water, all the available oxygen is used up. This causes oxygen dependent aquatic life to die. Thus, anaerobic bacteria (which do not require oxygen) begin to break down the organic waste and produce chemicals that have a foul smell and are

harmful to human health. Aerobic (oxygen requiring) bacteria degrade these organic wastes and keep the water depleted in dissolved oxygen.

Thus, the amount of oxygen required by bacteria to break down the organic matter present in a certain volume of a sample of water, is called **Biochemical Oxygen Demand (BOD)**. The amount of BOD in the water is a measure of the amount of organic material in the water, in terms of how much oxygen will be required to break it down biologically. Clean water would have BOD value of less than 5 ppm whereas highly polluted water could have a BOD value of 17 ppm or more.

(iii) Chemical Pollutants: As we know that water is an excellent solvent, water soluble inorganic chemicals that include heavy metals such as cadmium, mercury, nickel etc constitute an important class of pollutants. All these metals are dangerous to humans because our body cannot excrete them. Over the time, it crosses the tolerance limit. These metals then can damage kidneys, central nervous system, liver etc. Acids (like sulphuric acid) from mine drainage and salts from many different sources including raw salt used to melt snow and ice in the colder climates (sodium and calcium chloride) are water soluble chemical pollutants.

The organic chemicals are another group of substances that are found in polluted water. Petroleum products pollute many sources of water e.g., major oil spills in oceans. Other organic substances with serious impacts are the pesticides that drift down from sprays or runoff from lands. Various industrial chemicals like polychlorinated biphenyls, (PCBs) which are used as cleansing solvent, detergents and fertilizers add to the list of water pollutants. PCBs are suspected to be carcinogenic. Nowadays most of the detergents available are biodegradable. However, their use can create other problems. The bacteria responsible for degrading biodegradable detergent feed on it and grow rapidly. While growing, they may use up all the oxygen dissolved in water. The lack of oxygen kills all

other forms of aquatic life such as fish and plants. Fertilizers contain phosphates as additives. The addition of phosphates in water enhances algae growth. Such profuse growth of algae, covers the water surface and reduces the oxygen concentration in water. This leads to anaerobic conditions, commonly with accumulation of abnoxious decay and animal death. Thus, bloom-infested water inhibits the growth of other living organisms in the water body. This process in which nutrient enriched water bodies support a dense plant population, which kills animal life by depriving it of oxygen and results in subsequent loss of biodiversity is known as Eutrophication.

14.3.2 International Standards for Drinking Water

The International Standards for drinking water are given below and they must be followed.

Fluoride: For drinking purposes, water should be tested for fluoride ion concentration. Its deficiency in drinking water is harmful to man and causes diseases such as tooth decay etc. Soluble fluoride is often added to drinking water to bring its concentration upto 1 ppm or 1 mg dm^{-3}. The F^- ions make the enamel on teeth much harder by converting hydroxyapatite, $[3(Ca_3(PO_4)_2.Ca(OH)_2]$, the enamel on the surface of the teeth, into much harder fluorapatite, $[3(Ca_3(PO_4)_2.CaF_2]$. However, F^- ion concentration above 2 ppm causes brown mottling of teeth. At the same time, excess fluoride (over 10 ppm) causes harmful effect to bones and teeth, as reported from some parts of Rajasthan.

Lead: Drinking water gets contaminated with lead when lead pipes are used for transportation of water. The prescribed upper limit concentration of lead in drinking water is about 50 ppb. Lead can damage kidney, liver, reproductive system etc.

Sulphate: Excessive sulphate (>500 ppm) in drinking water causes laxative effect, otherwise at moderate levels it is harmless.

Nitrate: The maximum limit of nitrate in drinking water is 50 ppm. Excess nitrate in drinking water can cause disease such as methemoglobinemia ('blue baby' syndrome).

Table 14.2 Maximum Prescribed Concen-tration of Some Metals in Drinking Water.

Metal	Maximum concentration (ppm or mg dm^{-3})
Fe	0.2
Mn	0.05
Al	0.2
Cu	3.0
Zn	5.0
Cd	0.005

Other metals: The maximum concentration of some common metals recommended in drinking water are given in Table 14.2.

Activity 2

You can visit local water sources and observe if the river/lake/tank/pond are unpolluted/slightly polluted/ moderately polluted or severely polluted by looking at water or by checking pH of water. Document the name of the river and the nearby urban or industrial site from where the pollution is generated. Inform about this to Pollution Control Board's office set up by Government to measure pollution levels. Ensure that appropriate action is taken. You can write to the press also. Do not dump waste into a household or industrial drain which can enter directly to any water body, such as, river, pond, stream or lake. Use compost instead of chemical fertilizers in gardens. Avoid the use of pesticides like DDT, malathion etc., at home

and try to use dried neem leaves to help keep insects away. Add a few crystals of potassium permanganate ($KMnO_4$) or bleaching powder to the water tank of your house.

14.4 SOIL POLLUTION

India being an agriculture based economy gives high priority to agriculture, fisheries and livestock development. The surplus production is stored by governmental and non-governmental organisations for the lean season. The food loss during the storage also needs special attention. Have you ever seen the damages caused to the crops, food items by insects, rodents, weeds and crop diseases etc? How can we protect them? You are acquainted with some insecticides and pesticides for protection of our crops. However, these insecticides, pesticides and herbicides cause soil pollution. Hence, there is a need for their judicious use.

14.4.1 Pesticides

Prior to World War II, many naturally occurring chemicals such as nicotine (by planting tobacco plants in the crop field), were used as pest controlling substance for major crops in agricultural practices.

During World War II, DDT was found to be of great use in the control of malaria and other insect-borne diseases. Therefore, after the war, DDT was put to use in agriculture to control the damages caused by insects, rodents, weeds and various crop diseases. However, due to adverse effects, its use has been banned in India.

Pesticides are basically synthetic toxic chemicals with ecological repercussions. The repeated use of the same or similar pesticides give rise to pests that are resistant to that group of pesticides thus making the

pesticides ineffective. Therefore, as insect resistance of DDT increased, other organic toxins such as Aldrin and Dieldrin were introduced in the market by pesticide industry. Most of the organic toxins are water insoluble and non-biodegradable. These high persistent toxins are, therefore, transferred from lower trophic level to higher trophic level through food chain (Fig.14.3). Over the time, the concentration of toxins in higher animals reach a level which causes serious metabolic and physiological disorders.

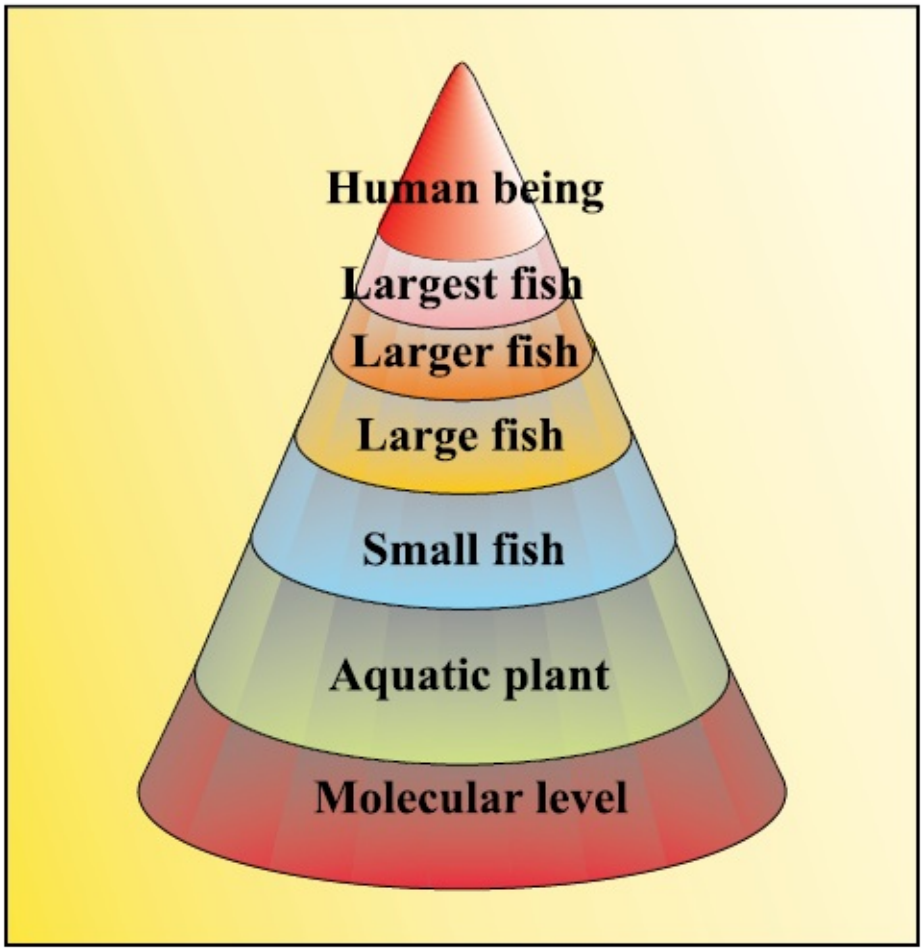


Fig. 14.3 At each trophic level, the pollutant gets 10 times concentrated.

In response to high persistence of chlorinated organic toxins, a new series of less persistent or more bio-degradable products called organo-phosphates and carbamates have been introduced in the market. But

these chemicals are severe nerve toxins and hence more harmful to humans. As a result, there are reports of some pesticides related deaths of agricultural field workers. Insects have become resistant to these insecticides also. The insecticide industry is engaged in developing new groups of insecticides. But one has to think, is this the only solution to pest menace?

These days, the pesticide industry has shifted its attention to herbicides such as sodium chlorate ($NaClO_3$), sodium arsinite (Na_3AsO_3) and many others. During the first half of the last century, the shift from mechanical to chemical weed control had provided the industry with flourishing economic market. But one must remember that these are also not environment friendly.

Most herbicides are toxic to mammals but are not as persistent as organo-chlorides. These chemicals decompose in a few months. Like organo-chlorides, these too become concentrated in the food web. Some herbicides cause birth defects. Studies show that corn-fields sprayed with herbicides are more prone to insect attack and plant disease than fields that are weeded manually.

Pesticides and herbicides represent only a very small portion of widespread chemical pollution. A large number of other compounds that are used regularly in chemical and industrial processes for manufacturing activities are finally released in the atmosphere in one or other form.

14.5 INDUSTRIAL WASTE

Industrial solid wastes are also sorted out as biodegradable and non-degradable wastes. Biodegradable wastes are generated by cotton mills, food processing units, paper mills, and textile factories.

Non-biodegradable wastes are generated by thermal power plants which

produce fly ash; integrated iron and steel plants which produce blast furnace slag and steel melting slag. Industries manufacturing aluminium, zinc and copper produce mud and tailings. Fertilizer industries produce gypsum. Hazardous wastes such as inflammables, composite explosives or highly reactive substances are produced by industries dealing in metals, chemicals, drugs, pharma-ceuticals, dyes, pesticides, rubber goods etc.

The disposal of non-degradable industrial solid wastes, if not done by a proper and suitable method, may cause serious threat to the environment. New innovations have led to different uses of waste material. Nowadays, fly ash and slag from the steel industry are utilised by the cement industry. Large quantities of toxic wastes are usually destroyed by controlled incineration, whereas small quantities are burnt along with factory garbage in open bins. Moreover, solid wastes if not managed effectively, affect the components of the environment.

Do you know about waste recycling?

• Fuel obtained from plastic waste has high octane rating. It contains no lead and is known as “green fuel”.

• Due to recent developments made in chemical and textile industries, clothes will be made from recycled plastic waste. These will be available soon in the global textile market.

• In India, our cities and towns face endless hours of power cut. We can also see piles of rotting garbage here and there. There is a good news that we can get rid from both these problems simultaneously. Technology has now been developed to produce electricity from the garbage. A pilot plant has been set up, where after removing ferrous metals, plastic, glass, paper etc. from garbage, it is mixed with water. It is then cultured with bacterial species for producing methane, commonly known as biogas. The remaining product is used as

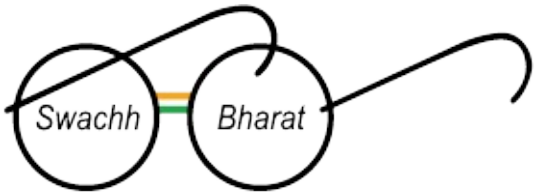
manure and biogas is used to produce electricity.

14.6 STRATEGIES TO CONTROL ENVIRONMENTAL POLLUTION

After studying air, water, soil and industrial waste pollution in this unit, by now you must have started feeling the need of controlling environmental pollution: How can you save your immediate environment? Think of the steps/activities, which you would like to undertake for controlling air, water, soil and industrial waste pollution in your neighbourhood. Here, an idea about the strategies for the management of waste is given.

14.6.1 Waste Management

Solid waste is not the only waste, which you see in your household garbage box. Besides household discards, there are medical, agricultural, industrial and mining wastes. The improper disposal of wastes is one of the major causes of environmental degradation. Therefore, the management of wastes is of utmost importance.



Ek Kadam Swachchhta ki or

You must be aware of the ‘Swachh Bharat Abhiyan’ or ‘Clean India Mission’ launched by the Government of India.

Two programmes are being implemented under the broad umbrella of the Swachh Bharat Abhiyan. These are Swachh Bharat Mission–Urban (SBM–U) and Swachh Bharat Mission Gramin (SBM–G). The SBM–U

primarily aims at making Urban India free from open defecation and achieving 100% scientific management of solid waste in the country. The SBM–G targets to bring about an improvement in the general quality of life in rural areas by promoting cleanliness and hygiene, and eliminating open defecation. It is accelerating its efforts to achieve the goal of universal sanitation coverage by 2 October, 2019, which is the birth aniversary of Mahatma Gandhi. If you have participated in some event on Swachh Bharat Mission, write your experiences.

Collection and Disposal

Domestic wastes are collected in small bins, which are then transferred to community bins by private or municipal workers. From these community bins, these are collected and carried to the disposable site. At the site, garbage is sorted out and separated into biodegradable and non-biodegradable materials. Non-biodegradable materials such as plastic, glass, metal scraps etc. are sent for recycling. Biodegradable wastes are deposited in land fills and are converted into compost.

The waste if not collected in garbage bins, finds its way into the sewers. Some of it is eaten by cattle. Non-biodegradable wastes like polythene bag, metal scraps, etc. choke the sewers and cause inconvenience. Polythene bags, if swallowed by animals can cost their lives also.

As a normal practice, therefore, all domestic wastes should be properly collected and disposed. The poor management causes health problems leading to epidemics due to contamination of ground water. It is specially hazardous for those who are in direct contact with the waste such as rag pickers and workers involved in waste disposal, as they are the ones who handle waste materials mostly without protective device such as gloves or water proof boots and gas masks. What can you do for them?

14.7 GREEN CHEMISTRY

14.7.1 Introduction

It is well known fact that self-sufficiency in food has been achieved in India since late 20th century by using fertilizers and pesticides and exploring improved methods of farming, good quality seeds, irrigation etc. But over-exploitation of soil and excessive use of fertilizers and pesticides have resulted in the deterioration of soil, water and air.

The solution of this problem does not lie in stopping the process of development that has been set in; but to discover methods, which would help in the reduction of deterioration of the environment. Green chemistry is a way of thinking and is about utilising the existing knowledge and principles of chemistry and other sciences to reduce the adverse impact on environment. Green chemistry is a production process that would bring about minimum pollution or deterioration to the environment. The byproducts generated during a process, if not used gainfully, add to the environmental pollution. Such processes are not only environmental unfriendly but also cost-ineffective. The waste generation and its disposal both are economically unsound. Utilisation of existing knowledge base for reducing the chemical hazards along with the developmental activities is the foundation of green chemistry. Have you perceived the idea of green chemistry? It is well known that organic solvents such as benzene, toluene, carbon tetrachloride etc., are highly toxic. One should be careful while using them.

Nobel goes to Green Chemists



Yves Chauvin



Robert H. Grubbs



Richard R. Schrock

Yves Chauvin, Institut Français du Pétrole, Rueil-Malmaison France, **Robert H. Grubbs** California Institute of Technology (Caltech), Pasadena, CA, USA and **Richard R. Schrock** Massachusetts Institute of Technology (MIT), Cambridge, MA, USA won the 2005 Nobel Prize in chemistry for work that reduces hazardous waste in creating new chemicals. The trio won the award for their development of the metathesis method in organic synthesis – a way to rearrange groups of atoms within molecules that the Royal Swedish Academy of Sciences likened to a dance in which couples change partners. The metathesis has tremendous commercial potential in the pharmaceuticals, biotechnology and food stuffs production industries. It is also used in the development of revolutionary environmentally-friendlier polymers.

This represents a great step forward for ‘green chemistry’, reducing potentially hazardous waste through smarter production. Metathesis is an example of how important application of basic science is for the benefit of man, society and the environment.

As you know, a chemical reaction involves reactants, attacking reagents and the medium in which the reaction takes place. Extent of any reaction depends upon physical parameters like temperature, pressure and use of catalyst. In a chemical reaction, if reactants are fully converted into useful environmental friendly products by using an environment friendly medium

then there would be no chemical pollutants introduced in the environment.

During a synthesis, care must be taken to choose starting materials that can be converted into end products with yield approximately upto 100 per cent. This can be achieved by arriving at optimum conditions of synthesis. It may be worthwhile to carry out synthetic reactions in aqueous medium since water has high specific heat and low volatility. Water is cost effective, noninflammable and devoid of any carcinogenic effects.

14.7.2 Green Chemistry in day-to-day Life

(i) Dry Cleaning of Clothes

Tetra chlroroethene ($Cl_2C=CCl_2$) was earlier used as solvent for dry cleaning. The compound contaminates the ground water and is also a suspected carcinogen. The process using this compound is now being replaced by a process, where liquefied carbondioxide, with a suitable detergent is used. Replacement of halogenated solvent by liquid CO_2 will result in less harm to ground water.

These days hydrogen peroxide (H_2O_2) is used for the purpose of bleaching clothes in the process of laundary, which gives better results and makes use of lesser amount of water.

(ii) Bleaching of Paper

Chlorine gas was used earlier for bleaching paper. These days, hydrogen peroxide (H_2O_2) with suitable catalyst, which promotes the bleaching action of hydrogen peroxide, is used.

(iii) Synthesis of Chemicals

Ethanal (CH_3CHO) is now commercially prepared by one step oxidation of ethene in the presence of ionic catalyst in aqueous medium with a yield of 90%.

$$CH_2 = CH_2 + O_2 \xrightarrow[Pd(II)\,/\,Cu(II)\,(in\ water)]{Catalyst} CH_3CHO\,(90\%)$$

(iv) 'Green Solution' to Clean Turbid Water

Powder of kernel of tamarind seeds has been found to be an effective material to make municipal and industrial waste water clean. It is non-toxic, biodegradable and cost-effective material. This powder is usually discarded as agricultural waste. The present practice is to use alum to treat such water. It has been found that alum increases toxic ions in treated water and can cause diseases.

Green chemistry, in a nutshell, is a cost effective approach which involves reduction in material, energy consumption and waste generation.

Think it Over

What is our responsibility as a human being to protect our environment?

Some concepts, if followed by an individual, contribute towards a better quality of our environment and human life. Always set up a compost tin in your garden or any other place in your home and use it to produce manure for your plants to reduce the use of fertilizers. Use a cloth bag and avoid asking for plastic carry bags when you buy groceries, vegetables or any other item. See that all newspapers,

glass, aluminum and other items in your area are recycled. We might have to take little trouble to locate such dealers. We must realize that we do not have solutions for every problem but we can concentrate on issues, which we feel strongly about and can do some thing about. We should take care to put into practice whatever we preach. Always remember environment protection begins with us.

Summary

Environmental chemistry plays a major role in environment. Chemical species present in the environment are either naturally occurring or generated by human activities. Environmental pollution is the effect of undesirable changes in the surrounding that have harmful effects on plants, animals and human beings. Pollutants exist in all the three states of matter. We have discussed only those pollutants, which are due to human activities, and can be controlled. Atmospheric pollution is generally studied as tropospheric and stratospheric pollution. Troposphere is the lowest region of the atmosphere (~10 km) in which man along with other organisms including plants exist. Whereas stratosphere extends above troposphere up to 50 km above sea level. Ozone layer is one of the important constituents of stratosphere. Tropospheric pollution is basically due to various oxides of sulphur, nitrogen, carbon, halogens and also due to particulate pollutants. The gaseous pollutants come down to the earth in the form of acid rain. 75% of the solar energy reaching earth is absorbed by the earth surface and rest is radiated back to the atmosphere. These gases mentioned above trap the heat which result into global warming. It is important to realise that these very gases are also responsible for the life on the earth as they trap the requisite amount of solar energy for the sustainance of life. The increase in the greenhouse gases is raising the temperature of the earth's atmosphere which, if not checked, may eventually result in melting of polar ice caps and consequently may submerge the costal land mass. Many human activities are producing chemicals, which are responsible for the depletion of ozone layer in the stratosphere,

leading to the formation of ozone hole. Through the ozone hole, ultraviolet radiations can penetrate into the earth's atmosphere causing mutation of genes. Water is the elixir of life but the same water, if polluted by pathogens, organic wastes, toxic heavy metals, pesticides etc., will turn into poison. Therefore, one should take care to follow international standards to maintain purity levels of drinking water. Industrial wastes and excessive use of pesticides, result into pollution of land mass and water bodies. Judicious use of chemicals required for agricultural practices can lead to sustainable development. Strategies for controlling environmental pollution can be: (i) waste management i.e., reduction of the waste and proper disposal, also recycling of materials and energy, (ii) adopting methods in day-to-day life, which results in the reduction of environmental pollution. The second method is a new branch of chemistry, which is in its infancy known as green chemistry. It utilizes the existing knowledge and practices so as to bring about reduction in the production of pollutants.

EXERCISES

14.1 Define environmental chemistry.

14.2 Explain tropospheric pollution in 100 words.

14.3 Carbon monoxide gas is more dangerous than carbon dioxide gas. Why?

14.4 List gases which are responsible for greenhouse effect.

14.5 Statues and monuments in India are affected by acid rain. How?

14.6 What is smog? How is classical smog different from photochemical smogs?

14.7 Write down the reactions involved during the formation of photochemical smog.

14.8 What are the harmful effects of photochemical smog and how can they be controlled?

14.9 What are the reactions involved for ozone layer depletion in the stratosphere?

14.10 What do you mean by ozone hole? What are its consequences?

14.11 What are the major causes of water pollution? Explain.

14.12 Have you ever observed any water pollution in your area? What measures would you suggest to control it?

14.13 What do you mean by Biochemical Oxygen Demand (BOD)?

14.14 Do you observe any soil pollution in your neighbourhood? What efforts will you make for controlling the soil pollution?

14.15 What are pesticides and herbicides? Explain giving examples.

14.16 What do you mean by green chemistry? How will it help decrease environmental pollution?

14.17 What would have happened if the greenhouse gases were totally missing in the earth's atmosphere? Discuss.

14.18 A large number of fish are suddenly found floating dead on a lake. There is no evidence of toxic dumping but you find an abundance of phytoplankton. Suggest a reason for the fish kill.

14.19 How can domestic waste be used as manure?

14.20 For your agricultural field or garden you have developed a compost producing pit. Discuss the process in the light of bad odour, flies and recycling of wastes for a good produce.

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